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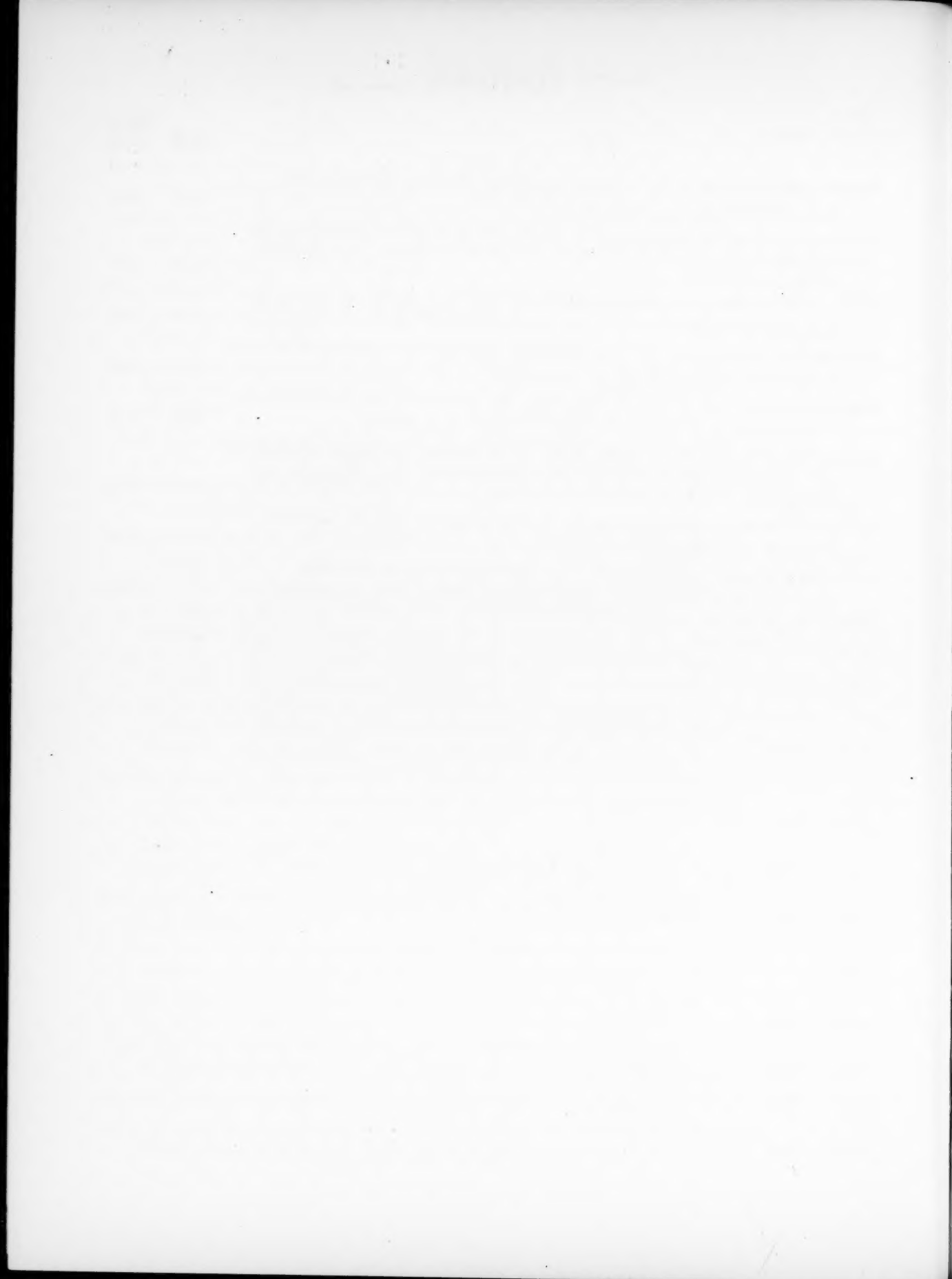
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Stepan Nikolaevich Danilov

Highly esteemed and dear Stepan Nikolaevich,

The Editorial Staff of "The Journal of General Chemistry," its authors and its readers congratulate you warmly on your seventieth birthday, forty-fifth anniversary of your scientific teaching activities and fortieth anniversary of your association with the editorial staff of the Journal and wish you good health for many years to come and further fruitful work to the good of our Motherland and Soviet science.

STEPAN NIKOLAEVICH DANILOV

N. A. Domnin

(For his seventieth birthday and the forty-fifth anniversary of his scientific and teaching activity)

In January 1959 the Soviet chemical world will be celebrating the 70th birthday and the forty-fifth anniversary of the scientific, teaching and social activity of one of the great scientists of our nation, Correspondent Member of the Academy of Sciences, USSR, Stepan Nikolaevich Danilov.

S. N. Danilov belongs to the celebrated scientific chemical school of Butlerov and Favorskii. Being a very erudite and progressive scientist, S. N. has been developing successfully the remarkable ideas and traditions of this school for the last 45 years. On the other hand, the most characteristic feature of all S. N.'s activity has been the relation between his theoretical work and practical problems and the development of new and existing aspects of science and technology.

When S. N. Danilov completed his diploma work in 1914 in the department of Physics and Mathematics (Natural Science Division), St. Petersburg University, under the guidance of A. E. Favorskii, he continued his work in Favorskii's laboratory as one of the latter's closest colleagues. In this period S. N. assisted at lectures, conducted seminar work for the course on organic chemistry, directed diploma candidates and the students' scientific chemical club. Working with great productive enthusiasm, he was an example to young chemists. Beginning in 1924, S. N. gave a series of special courses at the University on the theoretical bases of organic chemistry, heterocyclic compounds and carbohydrates and gave a series of lectures and reports on other fields of chemistry.

In connection with the wide development of industry and industrial chemistry in the Soviet Union in the twenties, S. N. showed a lively interest in industrial problems. From 1926, he directed the practical work of university students at factories for several years; from 1927-1931 he was a consultant to the Okhten chemical plant for the production of nitrocellulose, lacquers and plastics. This was the background to the invitation he received to become the professor and head of the department of artificial fibers, after its reorganization, when the Chemistry Department of the University was converted to the Leningrad Chemistry and Technology Institute. Later, this department was enlarged to include the chemical processing of cellulose. As director of this technological department for 28 years, S. N. trained a great number of highly qualified specialists in this very important field of chemistry.

In 1935 S. N. was awarded a Doctor's Degree in Chemistry, without having to defend his thesis, for his work on the isomeric conversions of aldehydes and hydroxyaldehydes. In 1943 he was elected correspondent Member of the Acad. Sci. USSR and in 1947 an Active Member of the Academy of Artillery Science.

From May 1945, at the request of the late Academician, A. E. Favorskii, S. N. became director of the departments of organic compound structures and highmolecular compounds of the Leningrad State University (L.S.U.). While directing the scientific research work of the two departments, S. N. was also director (1947-1949) of the Chemical Scientific Research Institute of Leningrad State University. In connection with the theoretical investigations of the University's Chemistry Faculty, during this period S. N. carried out extensive and fruitful work on problems of the chemical industry and initiated a reorganization of the research work being performed by the university chemists to bring it more in line with practical applications.

Besides studying theoretical problems of organic chemistry in A. E. Favorskii's laboratory from 1913 onwards, S. N. also worked in the State Institute of Applied Chemistry (1921-1927) and, as mentioned before, at

the Okhten chemical plant (1927-1930). During the period when S. N. worked in the Leningrad Technological Institute, he was also the scientific director of the cellulose laboratory at the Institute of Plastics (1931-1937) and at the affiliated Institute of the Ministry of Chemical Industry (1936-1941, 1944-1950).

Since 1949 S. N. has participated very actively in the organization of the Institute of High-Molecular Compounds of the Acad. of Sci. USSR and established the laboratory for work on the chemical reactions of cellulose and its derivatives, which he still directs. Since 1953 S. N. has been the director of the Institute of High-Molecular Compounds.

In 1918 S. N. was presented with the Mendeleev award for his outstanding work in the field of isomeric conversions and in 1930 — the Zinin and Voskresenskii award. The scientific contributions of S. N. have been valued highly by the Soviet Government and the Communist Party of the Soviet Union, who awarded him the Order of Lenin twice, the Order of the Red Banner of Labor, the Order of Merit and other medals. In 1944 S. N. was given the honorary title of Esteemed Worker in Science and Technology of the Tartar ASSR.

In addition to his extensive scientific, teaching and organizing-administrative activity, S. N. always participated in social work. Since 1916 he has been active in the D. I. Mendeleev All-Union Chemical Society and over the last few years, he has been chairman of the committee of the Leningrad Division of this society.

From 1918 to 1946 S. N. was assistant to the editor of the Journal of the Russian Physicochemical Society and the Journal of General Chemistry and since 1946 — the chief editor of the Journal of General Chemistry. We should note his exceptional interest in the supervisory work of the journal. Without exaggerating, one can state that S. N.'s attitude to this work has to a large extent helped win and consolidate the esteem that the Journal of General Chemistry commands in world chemical literature.

S. N.'s talent as a scientist and teacher, his original scientific ideas, love for science and creative enthusiasm have always attracted youth. He has trained about fifty candidates and doctors of science and not less than two thousand specialists, chemical engineers and chemical technologists.

As early as his student years, S. N. fully accepted Butlerov's ingenious ideas on the theory of chemical structure. As is known, Butlerov and Favorskii attached great importance to the study of isomerism for the further development of the theory of chemical structure. They considered that study of isomeric reactions, in particular, would produce most important data for solving the most complex and fundamental problems in the theory of chemical structure.

From the very beginning of his scientific activity, started under the direction of A. E. Favorskii, S. N. began to study isomeric reactions of such very reactive organic compounds as aldehydes, hydroxyaldehydes, sugars, etc. It should be noted that S. N. found his own original methods of investigation for his scientific work. All his works developed logically and consecutively and were based on clear definite ideas and purposes.

In 1917 S. N. was the first to discover the isomeric conversion of aldehydes to ketones, using triphenyl-acetaldehyde as the example [1-3].* In further investigations on the isomerization of aldehydes with tertiary and secondary groups to ketones, he used a series of examples and was later joined in this work by E. D. Venus-Danilova [1-9, 11-19, 25, 80, 106]. S. N. thoroughly studied the conditions for the isomeric conversions investigated by him and proposed mechanisms for them [101].

In his work, S. N. thoroughly studied the action of acid-alkali-salt catalysis under the conditions under which isomeric conversions of carbonyl and hydroxycarbonyl compounds occur. S. N. was the first to establish the connection between α -glycol dehydration and isomeric conversions of aldehydes and ketones into ketones and this was confirmed by his own work and by other authors.

In a general article [101], S. N. examined in detail the isomerization of aldehydes and ketones to ketones as a simultaneous oxidation-reduction reaction and compared it with α -glycol dehydration, hydration of acetylene hydrocarbons, isomerization of unsaturated alcohols to carbonyl compounds, α -oxide isomerization and other reactions.

Starting in 1925, S. N. and E. D. Venus-Danilova carried out a series of works on the isomerization of hydroxyaldehydes to hydroxyketones and acids through haloaldehydes and of the hydroxyaldehydes themselves.

* See p. 3209 for literature cited in this and the two following articles.

This reaction, first performed by S. N. as a hydroxyketone-saccharinic rearrangement, was confirmed by the reactions of several hydroxyaldehydes [20-22, 30, 38]. It was shown that isomerization of aldehydes of the aliphatic series may occur under the conditions of the dry distillation of wood [24]. It is important to note that the simplest models for epimeric conversions of monosaccharides, that had been known for a long time, were provided by S. N.'s work.

A study of the isomerization of haloaldehydes to acids made it possible for S. N. to explain correctly a number of works by other authors, who had explained them erroneously. On the other hand, the hypotheses S. N. put forward on the mechanism of glycol, aldehyde and hydroxyaldehyde reactions gave an opportunity to other authors to plan and carry out new experimental investigations.

S. N. and N. S. Tikhomirova-Sidorova together devoted some interesting work to the mechanism of hydroxyaldehyde reactions. In this work, the experimental data on the isomerization of hydroxyketones and chloroketones were confirmed for the first time polarographically [79, 93-95].

The very wide investigations S. N. carried out in the field of carbohydrates are closely related to his work on the isomeric reactions of aldehydes and hydroxyaldehydes. In the former field, he also obtained numerous, valuable results [26-28]. In 1936 S. N. and A. M. Gachokidze (50-52) worked out the isomerization of 2-bromoacetomonosaccharides to desonic acids. Later on Gachokidze successfully developed the work in this direction and obtained very interesting new data on isomeric reactions of monosaccharides and disaccharides.

S. N. and his colleagues achieved the epimerization of glucose and fructose by a new method - heating with pyridine, epimeric and degradative conversions of cellulose in the presence of lime, the acetolysis of cellulose, etc.

With I. S. Lishanskii, he investigated the amination and guanidination of monosaccharides, starting with their α -anhydrides [88, 89, 100]. These investigations gave a whole series of new and important facts, which served as a basis for new methods of synthesis in the sugar group. These works were valuable in connection with the chemistry of streptomycin.

Isomeric reactions of carbonyl and hydroxycarbonyl compounds are related to various biochemical processes of carbohydrates and were examined by S. N. in the light of concepts of inter- and intramolecular oxidation-reduction. These concepts can be widely used by physiologists and biochemists. S. N. himself proposed a simple scheme for the formation of lactic acid from glyceraldehyde through β -hydroxyoxide forms, similar to a saccharinic rearrangement.

S. N.'s investigations on the isomeric reactions of carbonyl and hydroxycarbonyl compounds have been generally accepted as classical and have brought him world recognition. One should note that in his works, directed mainly towards the study of isomeric reactions, S. N. also obtained extremely important and valuable material for developing the synthesis of many new substances as well as many unknown organic compounds.

Some of S. N.'s work was devoted to various syntheses in the field of lowmolecular compounds and of this work the following are the most important: the preparation of β -hydroxyketones by hydration of acetylene alcohols [33], syntheses of esters by V. E. Tishchenko's reaction [10], the synthesis of vinylcyclohexylcarbinol [49] and a convenient laboratory and technically suitable method of preparing benzyl ethers of glycerol and ethylene glycol, which are extremely valuable as plasticizers of cellulose esters [31, 41, 45]; together with his colleagues developed a synthesis of enanthol and undecylenic acid by decomposing esters of castor oil and, starting from the latter, prepared azelaic and sebacic acids [109, 110]; they discovered the reasons for poisoning of nickel catalysts by carbon monoxide during the hydrogenation of aliphatic oils [37] and investigated the reactions of amines with chloroamines [83].

S. N. initiated a study of the reaction of α -oxide rings with ammonia, water, hydrogen sulfide, etc [90] in the university laboratory. These reactions were later studied in detail by V. F. Martynov and are very valuable for the synthesis of antibiotics. S. N. also suggested that the reaction of nitrosyl chloride with olefins be investigated thoroughly [91] and this was carried out by K. A. Ogloblin.

S. N. has published monographs and critical reviews on molecular rearrangements [101, 129, 138], on the sequence and role of intermediate compounds in isomeric reactions [139], on sugar chemistry in Russia [136], on simultaneous oxidation-reduction reactions and molecular rearrangements [101, 137], etc. S. N. has also published

a large number of papers on the history of chemistry, contemporary problems in organic chemistry [114, 133-135] as well as some devoted to A. M. Butlerov [127-132], A. E. Favorskii [119-126], S. V. Lebedev [118], etc.

The wide and thorough investigations on isomeric reactions of carbonyl and hydroxycarbonyl compounds and the extensive theoretical and experimental material that S. N. had accumulated allowed him to turn to the study of high-molecular compounds such as polysaccharides, cellulose, viscose, etc. This change was not accidental, it was the culmination of a highly logical and successive development of ideas and concepts, worked out by S. N. in numerous investigations on isomeric reactions.

S. N. never tended to work out only the theoretical problems of science. The basis of S. N.'s methodology was, and is, the principle of the interrelation of theory and practice. This is fully confirmed by his wide and active participation in the development of various branches of the chemical industry. During the First and Second World War S. N. was wholly occupied with work connected with war requirements. All this together resulted in S. N.'s interest in high-molecular compounds, which have a tremendous theoretical and practical value.

Among S. N.'s works in the field of polysaccharides and cellulose, we should note those on cellulose, chitin, alginic acid and their derivatives. He investigated the various properties and methods of preparing cellulose ethers and esters, thoroughly studied the properties of nitrocelluloses and obtained new data for the development of the theory on cellulose nitration. In a study of the effect of acids [82, 104] and alkalis [117, 141] on cellulose, the formation of molecular compounds and the effect of swelling on the properties of hydro- and hydrated cellulose were established. In a study of the composition and vapor pressure of nitric acid in phosphoric-nitric acid mixtures, the relation of nitric acid vapor pressure to the presence of certain phosphoric acid hydrates was found [68]. It was shown that in treating cellophane with glycerol the cellulose took out the glycerol trihydrate, described by D. I. Mendeleev, from the aqueous glycerol [75]. It was shown that swelling and solution of cellulose in phosphoric acid was a new method of preparing heat-insulating materials of low specific gravity from cellulose and wood pulp [74]. A new method for characterizing the reducing capacities (copper numbers) of the hydrated cellulose fibers of a viscose filament compressed during extrusion was developed and involved heating the cellulose in Schweitzer's solution [67].

Extensive investigations were carried out on the conditioning of cellulose for the artificial fiber industry [32]. Surveys were published on the characteristics of cellulose [116] and on the determination of molecular weights [140]. It was established that in cuprammonium solutions of cellulose, there are molecular compounds of cellulose with bases, as in alkali cellulose [98, 103]. S. N.'s work provided new data on the synthesis of desoxy-cellulose, anhydrocellulose and cellulose esters, new methods of synthesis were found and the main properties of these almost unknown products characterized [102]. New data on the synthesis and properties of glycerol ethers of cellulose were obtained and the properties of soluble linear and cross-linked molecules of this ether described [66].

Using simple models, in his work S. N. examined the synthesis of plasticizers (benzoyl esters of ethylene glycol and glycerol), the synthesis of benzyl cellulose [41] and developed a more rapid method for determining the composition of benzyl ethers of cellulose by converting the benzyl groups to pentabromotoluene with aluminum and bromine [40]. The conditions for synthesizing carboxymethyl cellulose were studied [35] and this is now produced in large quantities in our factories for use as a lubricating material for boring and as detergents. The colloidal-chemical properties of ethyl and benzyl cellulose were characterized [46, 48]. Unsaturated ethers of cellulose were studied in connection with oxidation polymerization to form three-dimensional structures [78]. S. N. devoted a large number of papers to the study of nitrocellulose. The solution of cellulose nitroesters in various solvents was thoroughly investigated [70, 39]. The role of catalytic phenomena in the synthesis of cellulose esters and the synthesis of high-molecular compounds, in general, was examined critically [141].

A series of S. N.'s investigations were devoted to a study of alginic acid [99] and to the polysaccharide - chitin - which has been studied little [96, 97, 111]. He devoted extensive work to the chemistry and technology of viscose and cuprammonium spinning solutions. These investigations contain original data, which explain substantially the chemistry of viscose and cuprammonium solutions. The results of these works have been incorporated into text books on artificial fibers.

In this review we have noted only very briefly the most important work S. N. has carried out in various fields. A large number of papers describing work that was carried out at S. N.'s suggestion, under his direction and with his advice were published at various times under the names of his co-workers. Even from this brief review one can see how varied and productive S. N. Danilov's activities have been in the scientific, teaching, administrative-organization and social fields.

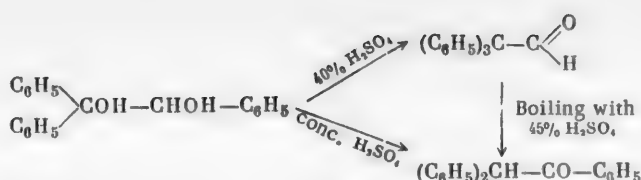
THE WORKS OF S. N. DANILOV IN THE FIELD OF ISOMERIC CONVERSIONS AND
MOLECULAR REARRANGEMENTS OF CARBONYL AND HYDROXYCARBONYL
COMPOUNDS AND CARBOHYDRATES AND THEIR
THEORETICAL IMPORTANCE

T. I. Temnikova, A. N. Anikeeva and N. S. Tikhomirova-Sidorova

During the 45 years since S. N. Danilov's first works on the problem of molecular rearrangements and isomeric conversions of oxygen-containing organic compounds, the concepts in this field of theoretical organic chemistry have evolved considerably. At present, one may consider it established that molecular rearrangements, complicating the course of basic chemical processes in organic chemistry (substitution, cleavage and addition), result from the kinetic tendency of the process to proceed with the migration of hydrogen atoms or hydrocarbon groups to adjacent positions; as regards equilibrium isomeric conversions, which in certain cases proceed very rapidly under the effect of catalysts specific for these conversions, they depend on the thermodynamic factor, as do all equilibrium processes.

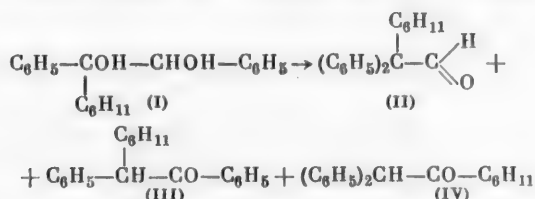
When in 1913, at the suggestion of his teacher, A. E. Favorskii, S. N. began the study of molecular rearrangements, observed during the treatment of α -glycols with mineral acids, many of the details of the concepts mentioned above were very unclear and the works of S. N. were very important in the development of contemporary ideas in these fields of theoretical organic chemistry. In spite of a series of quite convincing experimental data, at that time many investigators still believed in the formation of intermediates (oxides, full ethers of α -glycols and vinyl alcohols) in the rearrangement processes. The most outstanding foreign chemists, working in the field of molecular rearrangements (Tiffen and Meerwein), in examining the reasons why the reaction proceeded mainly or wholly in one of several theoretically possible directions, considered only the structure of the original glycol, the difference in stability of the bonds of the two hydroxyls and the different migration capacity of hydrocarbon groups; the latter was even considered a characteristic property of the group.

As a result of thorough, lucid work and brilliant experimental skill, S. N. Danilov, one of Favorskii's most talented students and faithful followers of the fundamental dialectic conceptions of Butlerov and Favorskii, not only solved a series of individual, confusing problems, but approached the investigation of this field in an essentially new way. Even in his first article devoted to the dehydration of secondary-tertiary α -glycols of hydrobenzoin derivatives [3], S. N. put forward a series of important suggestions, whose basic ideas recur through all the succeeding work: "The course of a reaction depends not only on radicals, but also on their interaction, on the dehydrating agent and on the conditions of the dehydration." As early as this article, he already states that "lability cannot be examined as a characteristic, independent value." He proved that the substance obtained earlier by Garder by treating phenylhydrobenzoin with HCl or HBr in an acetic acid solution and taken to be triphenylethylene oxide, was actually triphenylacetaldehyde [1, 3], while the substance obtained by Iakubovich by dehydrating allylhydrobenzoin, and considered by him to be the bimolecular full ether, was allyldiphenylacetaldehyde [4, 6] and S. N. not only established the structure of these substances, but also found conditions for the formation of either tri-substituted aldehydes or ketones during the rearrangement; he showed that triphenylacetaldehyde was obtained under more mild conditions and phenyldeoxybenzoin, under more drastic conditions and that under more drastic conditions, triphenylacetaldehyde was converted to phenyldeoxybenzoin [1, 3].



The aldehyde-ketone rearrangement, found for the aldehyde with a tertiary group, was then carried out in a series of works by S. N. and E. D. Venus-Danilova with other aldehydes, containing not only tertiary, but also secondary groups. It was found that isomerization may be induced by various acidic catalysts, dilute H_2SO_4 or a mixture of hydrochloric and acetic acid, and by mercury salts [8, 9, 11-14, 17, 18]. Similar reactions were soon noted in papers by M. Tiffen and A. P. Orekhov. Reaction with PCl_5 resulted in partial isomerization [4].

The discovery of the isomeric conversion of aldehydes to ketones — the Danilov aldehyde-ketone rearrangement — was of prime importance as it made it possible to examine more thoroughly the problem of the effect of conditions on the direction of α -glycol molecular rearrangement under the effect of an acid catalyst. In a detailed paper [12] on the dehydration of cyclohexylhydrobenzoin (I), it was shown that the direction of the rearrangement and the relative amount of possible reaction products [diphenylcyclohexylacetaldehyde (II), cyclohexyldeoxybenzoin (III) and benzhydrylcyclohexyl ketone (IV)] depended greatly on the process conditions and catalyst used.



Thus, the greatest aldehyde yield was obtained with oxalic acid; as the sulfuric acid concentration or the time of its effect increased the aldehyde and cyclohexyldeoxybenzoin contents decreased and that of benzhydrylcyclohexyl ketone increased; treatment with concentrated H_2SO_4 gave only the latter ketone. It is obvious from these data that the final result of the reaction does not depend on the structure of the original glycol but is determined by the conditions of the process. It was shown by separate experiments that treatment with conc. H_2SO_4 isomerized diphenylcyclohexylacetaldehyde (II) to benzhydrylcyclohexyl ketone (IV), i.e., to the ketone which is obtained as the sole product from the glycol under the same conditions.

In 1920 S. N. first put forward the idea that ketones, the same as aldehydes, could be converted to isomeric ketones; A. E. Favorskii and A. A. Chilingarian isomerized a ketone to another ketone, using as the example the conversion of isopropyl phenyl ketone to unsymmetrical methylphenylacetone; the ketone was isomerized by heating with ZnCl_2 at 350° , i.e., under considerably more drastic conditions than that used for α -glycol dehydration; in both cases, both with dehydration and isomerization, the processes terminated with the formation of the same ketone. Attempts to isomerize cyclohexyldeoxybenzoin to benzhydrylcyclohexyl ketone were unsuccessful. From this work, as well as from the data of earlier papers on the capacity of aldehydes to isomerize to ketones, S. N. came to the following conclusion: "if the dehydration product is a mixture of aldehyde and ketone, the ratio of the components in the given mixture may be changed by using more concentrated acid and greater heating" [12]. However, it did not follow from this that aldehydes always formed as intermediate products when α -glycols were treated with concentrated sulfuric acid; it could be assumed that conversion of α -glycols to ketones or aldehydes by treatment with concentrated sulfuric acid and, correspondingly with dilute sulfuric acid, proceeded by different mechanisms.

In order to find out whether any structurally stable substances — aldehydes, oxides or dioxane derivatives — form as intermediate products during the conversion of the α -glycol to the ketone, it is necessary to study the interrelations of all these compounds under the reaction conditions and the possibility of their interconversion. S. N. and E. D. Venus-Danilova undertook such an investigation by studying the interrelation between unsymmetrical methylphenylethylene glycol (I) and the anhydride forms corresponding to it — oxide (II), the full ether of the glycol as well as methylphenylacetaldehyde (III) and methyl benzyl ketones (IV) [18]. Treatment of the α -glycol with mineral acids gave, as in other cases, different carbonyl-containing compounds, depending on the conditions,

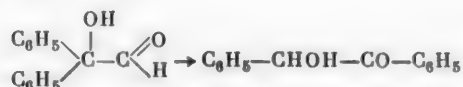
$$\begin{array}{ccccc}
 \text{C}_6\text{H}_5 & & \text{C}_6\text{H}_5 & & \text{C}_6\text{H}_5 \\
 & \diagup & & \diagdown & \\
 & \text{C} & & \text{C} & \\
 & \diagdown & & \diagup & \\
 \text{CH}_3 & & \text{CH}_3 & & \text{CH}_3
 \end{array}
 \begin{array}{c}
 \text{OH} \\
 | \\
 \text{CH}_2\text{OH}
 \end{array}
 \begin{array}{c}
 \xrightarrow[\text{conc. H}_2\text{SO}_4]{\text{dil. H}_2\text{SO}_4} \\
 \xrightarrow[\text{H}_2\text{SO}_4]{\text{dil. H}_2\text{SO}_4, \text{ heat}} \\
 \xrightarrow[\text{H}_2\text{SO}_4]{\text{conc. H}_2\text{SO}_4}
 \end{array}
 \begin{array}{c}
 \text{C}_6\text{H}_5 \\
 | \\
 \text{CH} \\
 | \\
 \text{C=O}
 \end{array}
 \begin{array}{c}
 \text{H} \\
 | \\
 \text{O}
 \end{array}
 \begin{array}{c}
 \text{(III)} \\
 \downarrow \text{conc. H}_2\text{SO}_4 \\
 \text{CH}_3-\text{CO}-\text{CH}_2-\text{C}_6\text{H}_5 \\
 \text{(IV)}
 \end{array}
 \begin{array}{c}
 \text{O} \\
 \diagup \quad \diagdown \\
 \text{C} \quad \text{CH}_2 \\
 \diagdown \quad \diagup \\
 \text{CH}_3
 \end{array}
 \begin{array}{c}
 \text{(II)}
 \end{array}$$
$$\begin{array}{c} \text{(CH}_3\text{)}_3\text{C-CHOH-COOH} \xrightarrow{\text{-HCOOH}} \\ \text{(CH}_3\text{)}_3\text{C-CH}_2\text{OH} \xrightarrow{\text{O}} \end{array} \rightarrow \text{(CH}_3\text{)}_3\text{C-C} \begin{array}{l} \text{O} \\ \text{//} \\ \text{H} \end{array} \rightarrow \text{(CH}_3\text{)}_2\text{CH-CO-CH}_3$$
$$(\text{C}_6\text{H}_5)_3\text{C}-\text{C} \begin{array}{l} \nearrow \text{NOH} \\ \searrow \text{H} \end{array} \xrightarrow[\text{H}^+]{\text{H}_2\text{O}} (\text{C}_6\text{H}_5)_3\text{C}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{H} \end{array} + (\text{C}_6\text{H}_5)_2\text{CH}-\text{CO}-\text{C}_6\text{H}_5$$

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were isomerized to ketones [24]; these observations showed that care had to be taken in interpreting the experimental data on pyrolysis of natural products which occur in the presence of ash, as certain of its components may act similarly as catalysts; as a result, ketones, isolated from the reaction mixture, may be formed by the isomerization of the initially formed aldehydes.

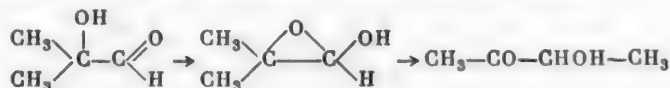
In 1925 S. N. and E. D. Venus-Danilova started a systematic study of the behavior of α -hydroxyaldehydes under the action of various types of catalysts. The work on α -hydroxyaldehydes in an acid medium is a logical continuation of the work on the isomerization of aldehydes to ketones; in addition it is closely related to the work of A. E. Favorskii and co-workers on the isomerization of α -ketoalcohols in an acid medium.

From the data given by Nef, who obtained acetyl- and benzoylcarbinols by hydrolyzing the acetals of lactic and mandelic acids, it was concluded that the simplest α -hydroxyaldehydes, which are isomerized to α -ketoalcohols with the transfer of two hydrogen atoms, are very labile. Therefore, it was most interesting to isomerize α -hydroxyaldehydes with a tertiary alcohol group, as in this case the rearrangement of the carbon skeleton of the molecule should occur. S. N. discovered hydroxyaldehyde - hydroxyketone isomerization on the example of the conversion of diphenylglycolaldehyde to benzoin by heating at 130-140° in an alcohol solution in the presence of a few drops of conc. H_2SO_4 [20].



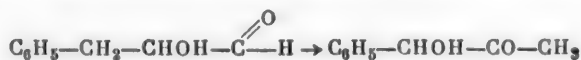
Thus, essentially, S. N. Danilov discovered a new form of isomeric conversion. Partial isomerization of diphenylglycolaldehyde also occurs when it is heated in an alkaline solution of copper hydroxide or an alcohol solution of mercuric chloride. In this case there is a considerable amount of benzil among the oxidation products of the hydroxyaldehyde. Later on α -hydroxyisobutyraldehyde and dicyclohexylglycolaldehyde were isomerized similarly [21, 22].

According to S. N. Danilov and E. D. Venus-Danilova, hydroxyaldehyde - hydroxyketone rearrangement in an acid medium proceeds with the intermediate formation of α -hydroxy oxides.



The same type of mechanism was proposed by A. E. Favorskii for the isomeric conversion of α -ketoalcohols in an acid medium. Quite recently, the hypothesis on the intermediate formation of α -hydroxy oxides was confirmed by the work of T. I. Temnikova and E. N. Kropacheva, using the isomerization of α -methoxy oxides as an example; however, taking into account the catalytic effect of sulfuric acid on these conversions, one should consider the participation of the proton, coordinately bound to the oxygen atom. It is possible that a similar scheme is also applicable to catalysis with metal salts that are capable of complex formation. S. N. proposed a mechanism for processes catalyzed by alkali solutions of cupric oxide, which is similar to the mechanism of other oxidation-reduction reactions (the reactions of Cannizzaro, V. E. Tishchenko and Meerwein and Ponderff).

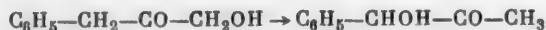
The next stage in S. N.'s work was the study of the stability of α -hydroxyaldehydes, which have a secondary alcohol group and are homologs of the extremely labile, simplest α -hydroxyaldehydes, that is mandelo- and lactaldehyde. He found that secondary α -hydroxyaldehydes in an alcohol - sulfuric acid medium were more completely isomerized: instead of the expected primary α -ketoalcohol, benzylglycolaldehyde gave phenylacetylcarbinol [29].



A similar conversion was observed later by E. D. Venus-Danilova and V. F. Kazimirova, who obtained methylacetylcarbinol by isomerizing α -hydroxybutyraldehyde.

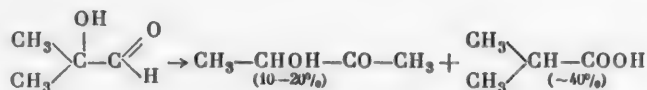
In order to establish the mechanism of these interesting rearrangements which could not be explained by alcohol-oxide schemes, it was necessary to find out whether α -ketoalcohols, containing a primary alcohol group,

were converted to isomeric α -ketoalcohols with a secondary alcohol group with the position of the carbonyl unchanged (1,3-rearrangement), for example



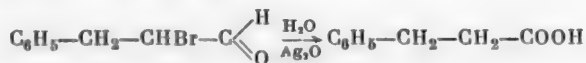
The formation of primary α -ketoalcohols from α -hydroxyaldehydes is quite probable as this type of conversion is well known for monosaccharides (epimerization). However, S. N. Danilov and N. S. Tikhomirova-Sidorova established that the primary α -ketoalcohols, $\text{C}_6\text{H}_5\text{CH}_2\text{CO}-\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2-\text{CO}-\text{CH}_2\text{OH}$, are not isomerized under the conditions used for conversion of hydroxyaldehydes to secondary α -ketoalcohols [94]. Thus, the mechanism of the deep isomerization of secondary α -hydroxyaldehydes remains unexplained.

α -Hydroxyisobutyraldehyde is only partially isomerized to a hydroxyketone in the presence of an alkali solution of copper hydroxide. The main product is isobutyric acid which is formed as a result of an isomeric acid conversion [34]; this type of rearrangement, similar to the saccharinic rearrangement, is well known for monosaccharides.



Without cupric oxide in the alkali medium, the α -hydroxyaldehydes, in contrast to a monosaccharide, are converted by Cannizzaro's reaction to a mixture of α -hydroxyacids and α -glycols. Only α -hydroxyaldehydes with a tertiary hydroxyl are capable of acid conversion.

The work on isomeric conversions of α -hydroxyaldehydes to α -hydroxyketones or to saturated acids is closely connected with S. N.'s investigations in the field of α -haloaldehydes in the presence of alkali solutions of heavy metal hydroxides. Haloaldehyde conversions are similar to those of α -hydroxyaldehydes, which are related to them genetically. In many cases, hydroxyaldehydes and bromoaldehydes were investigated in parallel. Using α -bromodicyclohexylacetaldehyde and α -bromobenzylacetaldehyde as examples, S. N. Danilov and E. D. Venus-Danilova demonstrated the possibility of almost quantitative conversion of bromoaldehydes to saturated acids by heating them with water and silver oxide [23, 29].



These investigations, on the other hand, are the direct continuation and development of the work of A. E. Favorskii and co-workers on the acid conversion of haloketones.

The mechanism of the conversions of haloaldehydes and haloketones to saturated acids are, most probably, similar. In this case, isomeric conversion does not occur, but substitution of the halogen atom by a hydroxyl, complicated by the rearrangement of the reacting molecule's skeleton. In such processes deeper changes in the skeleton may occur than in isomeric conversions. Thus, S. N. Danilov and N. S. Tikhomirova-Sidorova proved that extensive rearrangement may occur in replacing the chlorine in α -chloroketones by a hydroxyl [79]. Heating 1-chlorobutanone-2 with an alkali solution of potassium plumbite gave a mixture of propionyl- and methylacetylcarbinols.

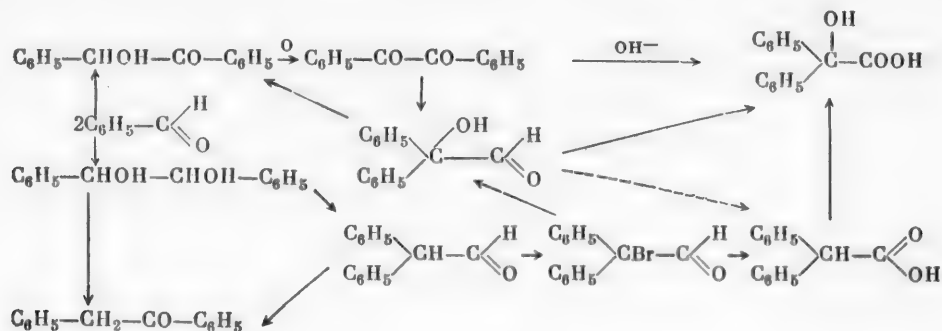


As mentioned above, special experiments showed that primary alcohols are not converted to secondary ones [94].

All the isomeric conversions studied are intramolecular oxidation-reduction processes. It seemed interesting to apply the polarographic method to evaluating the reducing capacity of isomeric ketoalcohols and chloroketones. Comparison of the polarographic characteristics of 1-chloro- and 3-chlorobutanones-2 and those of the α -ketoalcohols corresponding to them, showed that the capacity for reduction of the primary chloroketone is less than that of the secondary; in the case of ketoalcohols the reverse is the case: methylacetylcarbinol is reduced more readily than propionylcarbinol [94].

The various types of isomeric conversions and molecular rearrangements studied by S. N. may be summarized

by the following general scheme for the transitions of genetically interrelated substances; the scheme uses as an example compounds with two phenyl groups and two carbons in the chain and is completed by data from other authors.

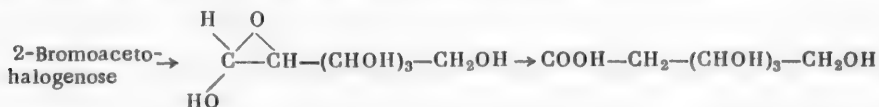


The types of conversion, first carried out by S. N. are shown by the darker arrows; isomerization of a hydroxy-aldehyde, using diphenylglycolaldehyde as the example, was predicted (marked by dashes); a similar reaction was carried out using α -hydroxyisobutyraldehyde.

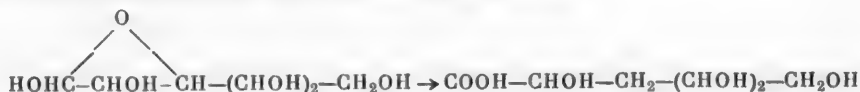
It is interesting to examine briefly the characteristics of the salt catalysts (heavy metal salts) that S. N. used widely in studying isomeric conversions. Salt catalysts and, in certain cases, concentrated sulfuric acid, have a double effect: on the one hand they form quite labile complex compounds with the starting materials and thus facilitate isomeric conversion; on the other hand, as they are more stably and complexly bound with the isomerized molecules, they stabilize the latter; as a result the position of the equilibrium is determined, not by the stability of the compounds themselves, but by the relative stability of the complexes with the catalyst. According to S. N., this is the reason for the formation of the same substances in different processes which use the same catalysts (for example, mercury salts) [101].

The numerous and varied works S. N. carried out in the field of monosaccharides and disaccharides was the logical continuation of his investigations on the isomeric conversions of α -hydroxycarbonyl compounds. Having carried out the acid conversion of α -bromoaldehydes and α -hydroxyaldehydes, S. N. put forward the hypothesis that a bromo-2-aldohehexose may be converted to a desonic type of acid or, in other words, an orthosaccharinic acid [50, 52]. Formulas were derived for all the theoretically possible saccharinic acids on the assumption that in an alkaline medium, forms with ethylene oxide, propylene oxide and hexylene oxide rings are produced, which are in a definite equilibrium with the more stable forms, pyranose and furanose, and the less stable form with a free carbonyl group.

Desonic acids may be formed from halogen monosaccharides by the scheme:



Other saccharinic acids with an unbranched carbon skeleton and a methylene group, which are called stereoisomers of metasaccharinic acid, may be formed by the scheme:



The formation of other saccharinic acids may be represented similarly. S. N. considered that acids with branched skeletons formed from ketoses.

Under the conditions for isomerizing α -bromoaldehydes and α -hydroxyaldehydes (α -hydroxyisobutyraldehyde and others) to acids, S. N. and A. M. Gachokidze obtained glucodesonic acid from 2-bromotriacetylglucose by

heating it with lead oxide and trimethylglucodesonic acid from bromotrimethylglucose [50, 52]. This reaction was later studied by A. M. Gachokidze using as examples galactoses, L-arabinoses, D-xyloses, D-arabinoses, lactoses, cellobioses and maltoses.

The development of the synthesis of orthosaccharinic acids is a valuable contribution in the field of molecular rearrangements and to sugar chemistry.

The epimeric conversions of carbohydrates are also closely related to the isomeric conversions of hydroxy-carbonyl compounds. Glucose and fructose were epimerized by S. N., E. D. Venus-Danilova and P. S. Shantarovich, by a new method: heating in dry pyridine [27]. In contrast to the previous methods using mineral hydroxides, under the new conditions no mannose or saccharinic acids were formed; there was no cleavage to lactic acid which indicates the specificity of the catalyst. In the presence of moisture in the pyridine, mannose is formed in the glucose-fructose mixture. According to S. N., the conversion proceeds by different schemes in the dry and in water-containing media as in one case the catalyst is the base itself, while in the moist medium it is a hydroxide of the ammonia type.

The new method of sugar epimerization, besides definite theoretical interest, was also of practical importance as it was widely used for the synthesis of previously unknown ketopentoses. This also fully confirmed S. N.'s conclusion on the specificity of the catalyst's effect. For example, Schmidt and Treiber prepared D-xylose without traces of altrose by heating D-xylose in dry pyridine. The investigations of Vargha, Levene and Hill also confirmed these data and conclusions. S. N. explained monosaccharide epimerization by the transposition of hydrogen and hydroxyl between the first and second carbon atoms with the help of catalysts.

In works by S. N. and P. T. Pastukhov [71, 73], it was shown that heating of maltose and cellobiose with pyridine did not induce the epimerization of these disaccharides to ketobioses; only anomeric conversion of the α - and β -forms occurred. However, in the presence of small amounts of lime the cellobiose gave β -(1,5)-D-glucosido-4-(1,5)-D-mannose. Cleavage of cellobiose to methylglyoxal was observed in more concentrated alkali solutions. In work on the acetolysis of cellulose [73], the conditions for obtaining the greatest yields of cellobiose were developed. The role of temperature, time, composition of the acetolysis mixture, water content of the cotton material and the amount and nature of the catalyst were clarified. The advantages of perchloric acid in comparison with sulfuric acid were shown. The former does not form esters with cellulose or its cleavage products and gives better yields of cellobiose octaacetate. The problem of designating α - and β -forms as cis- and trans-isomers was examined in the work. Being of practical importance, as it described the preparation of cellobiose under efficient conditions, this work also clarified the mechanism of acetolysis; namely, in cellulose acetolysis, acetic anhydride (acetic acid) is added by the links, binding the monosaccharide residues, and as a result these bonds are broken, while under these conditions the internal monosaccharide links are stable.

The problem of the configuration and reactivity of sugar anomers was examined in the work by S. N. and O. P. Koz'mina [105]. In studying the effect of phosphorus pentachloride on sugar the German chemist Brigl concluded that this reaction did not occur with high-melting cellobiose octaacetate or with α -glucose. Actually, the reaction occurs with α - and with β -form of sugar acetates but with different yields of the most stable tetrachloride. The investigations S. N. carried out in this field define more accurately the problem of the reactivity of various stereoisomeric sugar forms.

A considerable section of S. N.'s work is devoted to anhydrides, amino and guanido derivatives of carbohydrates and polyhydric alcohols. S. N. and L. S. Lishanskii [89, 100] studied the formation mechanism of α -oxides and the introduction of ammonia, methylamine and guanidine into a sugar molecule through an α -oxide ring. These investigations are valuable in the synthesis of streptomycin, which contains in its molecule a guanido derivative of inositol and a methylamino derivative of L-glucose. In connection with this, one should note that the American chemists Wolfram and Lemieux examined the conversion of a streptomycin molecule on the basis of the work by S. N. and E. D. Venus-Danilova on isomeric conversions of α -hydroxyaldehydes.

In order to find the best method for introducing a guanido group into monosaccharides, experiments were carried out in different directions including a study of the effect of S-methylisothiurea and O-methylisourea on 2-desoxy-2-amino-4,6-benzylidene- α -methylaltroside and 1,2-isopropylidene-6-desoxy-6-aminoglucose. This gave results which allowed a critical evaluation of the existing methods of guanidation and showed that the deciding factor in the reaction of S-methylisothiurea with the amine was the degree of basicity of the amine — the higher the basicity the more readily the guanidation proceeded.

TABLE

Simultaneous Oxidation-Reduction Reactions in the Carbohydrate Group and their Conversion Products

Intramolecular oxidation-reduction		Intermolecular oxidation-reduction			
monomolecular intramolecular oxidation-reduction I	polymolecular intramolecular oxidation-reduction II	hydrolytic and solvolytic cleavage III	hydration and alkaline oxidation-reduc- tion IV	dehydration and decarboxylation oxidation-re- duction V	desoxidation of carbohydrates VI
1. Tautomerism (enediols). 2. Isomerization of aldehydes and ketones and hydroxyaldehydes and hydroxyketones into hydroxyketones. 3. Epimerization of monosaccharides, Amadori rearrangement. 4. Saccharinic rearrangement: a) of monohydroxyaldehydes (hydroxyisobutyraldehyde into isobutyric acid), b) of monosaccharides c) of monohaloaldehydes, halo ketones and halo monosaccharides. 5. Isomerization of triose to lactic acid. 6. Conversions (inter) of aldehydes, pyranose and furanose forms, anomers. 7. Synthesis of inositol from hexoses (transfer of a hydrogen atom and cyclization of a biradical).	1. Hydrogen bonds (cellulose and nucleic acids). 2. Synthesis of monosaccharides by Butlerov's method, synthesis of oligosaccharides. 3. Polymerization of formaldehyde and α -oxides of glycidic alcohol. 4. Conversion of hexose into trioses and back. 5. Acyloin, benzoin, aldol and complex ether condensation of aldehydes.	1. Hydrolysis of oligosaccharides and polysaccharides. 2. Acetolysis, alcoholysis and mercaptolysis of polysaccharides.	1. Hydration of glucal into a desose 2. Hydration of anhydrosugars and anhydrides of polyhydric alcohols. 3. Cannizzaro reaction for aldehydes, hydroxyaldehydes and monosaccharides. 4. Benzil rearrangement. 5. Amination and guanidation of sugars.	1. Anhydrization of monosaccharides, disaccharides and polyatomic alcohols. 2. Anhydrides of cellulose (anhydrocellulose). 3. Formation of methylglyoxal from monosaccharides. 4. Decarboxylation (pyruvic acid) 5. Hydroxymethylfurfural, methylfurfural, furfural and maltol from carbohydrates.	1. Formation of methyloses and methylpentosans and desoses. 2. Desoxycellulose 3. Celluloseens and glucoseens. 4. Levulinic acid from hexoses (complex conversion). 5. Aromatization of carbohydrates (polyphenols).

From the experimental data the authors concluded that the guanidation mechanism proposed in the literature was incorrect. The effective initiator in guanidation is apparently cyanamide at the moment of evolution. It was then established that the action of alcoholic guanidine solutions on monosaccharide anhydrides at 100° is similar to the action of alkali metal alcoholates, i.e., an alcohol molecule is added by the oxide ring and no guanido derivative is formed. The authors considered that guanidine formed a molecular compound with alcohol and this was also confirmed by reacting monoacetylguanidine with the same anhydride (2,3-anhydro-4,6-benzylidene- α -methylalloside) in an alcohol solution. The main product was the same 2-methyl-4,6-benzylidene- α -methylaltroside, as in the first case. Under the experimental conditions guanidine hydrochloride was dissociated in an alcohol medium and the hydrogen chloride ruptured the anhydride ring to form 3-chloromonosaccharides. A different method was used for introducing the guanido group: the monosaccharide anhydride was heated in a pyridine solution of guanidine. Thus, a new, simple and convenient method for synthesizing carbohydrate guanido derivatives was demonstrated.

The work confirmed the rule that a *trans*-position of the adjacent hydroxyls is required for the formation of anhydro rings in sugars. There are several explanations for the need for a *trans*-configuration. S. N. Danilov gave one of the most probable explanations. He considers that the first stage in anhydro formation, under the action of alcoholates, is the addition of alcoholate to the free hydroxyl group. In the case of a *cis*-configuration this addition is greatly hindered by the effect (either electronegatively or simple-sterically) of the tosyl group. With a *trans*-configuration this phenomenon is much weaker. The alcoholate addition product formed then decomposes to give salts of the sulfonic acid and form the anhydride; inversion of the carbon atom, which bore the tosyl group, occurs. On the basis of experimental material and by generalizing literature data, S. N. put forward a general hypothesis on the factors affecting the direction of oxide ring rupture in monosaccharides and polyhydric alcohols, which he propounded in a report to the Kiev Conference on Problems of the Mechanism of Organic Reactions [93]. S. N. noted that the direction of rupture of the oxide ring is affected by: a) the position of the oxide ring relative to the plane of the pyran ring of the whole molecule, b) the α - or β -configuration of the first carbon atom and substituent on it and c) the character and position of other substituents in the molecule. These basic premises were confirmed by a series of experimental and literature facts.

Other investigations by S. N. et al. lead to the synthesis of a series of new derivatives of polyhydric alcohols and their anhydrides and monosaccharides. The chlorohydrin of 1,4-anhydroxylitol, which was first prepared by S. N. and V. F. Kazimirova [92], was the starting material for new derivatives. In the Institute of High-Molecular Compounds of the Acad. Sci. USSR, S. N. et al. [107] started from xylitol, xylitan and xylitan chlorohydrin and obtained their acetals, ketals, urethans, unsaturated ethers, amino derivatives and other compounds, which in their turn act as intermediates for the synthesis of new substances in the chemistry of high-molecular compounds.

In a brief summary one should note, in at least a few words, the work by S. N. and L. I. Rastorgueva [99] in which they developed a method of hydrolyzing alginic acid and obtained a series of new derivatives of manuronic acid. This work showed that, as is generally the case with polysaccharides, the products of alginic acid hydrolysis offer many possibilities for the synthesis of practically valuable substances in the difficult and interesting field of sugars and polyhydric alcohols.

In his numerous reports and lectures S. N. examined the conversion of oxygen-containing organic compounds as a simultaneous oxidation-reduction reaction. In 1949 [87] he put forward a strict classification of the oxidation-reduction reactions, having systematized and expanded them to cover many groups of compounds. Later [112] this classification was developed in greater detail, especially for hydroxycarbonyl compounds and carbohydrates, including cellulose, and this is shown in the table. Many of the types of oxidation-reduction reactions given in the table were carried out by S. N. et al. (I_{2,3,4}; III_{1,2}; IV₅; V_{1,2,3}; VI_{2,3}).

From the point of view of intramolecular oxidation-reduction, S. N. examined many biochemical reactions and, for example, explained the ripening of the product of glucose epimerization to the sweeter fructose [112].

The well-known reactions of carbonyl and hydroxycarbonyl compounds, carbohydrates and polyhydric alcohols discovered by S. N. Danilov open up many interesting directions and will be the object of new and numerous investigations in organic chemistry and the chemistry of high-molecular compounds.

THE WORKS OF S. N. DANILOV IN THE FIELD OF CELLULOSE AND ITS ETHERS AND ESTERS

E. A. Plisko, M. G. Okun', N. M. Grad and N. F. Gintse

The many-sided scientific activity of S. N. Danilov is closely connected with problems in the study of the chemistry of cellulose and its derivatives and also of alginic acid and chitin. New data were obtained on the behavior of cellulose towards solvents, on nitrocellulose, acetylcellulose and nitroacetylcellulose, on cellulose ethers and on the hydrolysis of alginic acid and the information on chitin extended.

These works were developed in the early 30s in the laboratory of the Leningrad Technological Institute, Leningrad (L.T. I.) and lately, investigations are being carried out on other polysaccharides, as well as cellulose, in the High-Molecular Compound Institute of the Acad. Sci. USSR.

In joint work, S. N. and N. F. Gintse studied the effect of various conditions on the solubility of cellulose in phosphoric acid [104] and found that the solubility curve of cellulose in strong phosphoric acid relative to acid concentration had two maxima, corresponding to regions of unlimited swelling with an intermediate region of incomplete solubility between them. The positions of the maxima corresponded to those acid concentrations at which the acid existed in the form of a monohydrate and a polyhydrate. These facts indicate the essential role of hydrates in the solution of cellulose in concentrated electrolyte solutions. Preliminary activation of the cellulose with water or dilute phosphoric acid made it possible to achieve complete solution of the cellulose material along the whole length of the curve, including the intermediate region between the maxima.

The role and the effect of hydrates was reported in another work by S. N. et al. on the study of the properties and vapor pressure of nitric acid in phosphoric-nitric acid mixtures [68]. In these mixtures, the course of the vapor pressure-composition curves is conditioned by the decomposition of nitric acid hydrates in the presence of phosphoric acid. The dehydrating effect of phosphoric acid appears only as a strong retardation of the fall in nitric acid vapor pressure, while for mixtures of sulfuric acid nitric acids and water, over a certain range of concentrations there is an increase in pressure to a maximum and a subsequent fall, which is explained by the stability of the monohydrates and even the dihydrates of sulfuric acid. Phosphoric acid was shown to contain a stable hydrate only with a content of 1 molecule of water to two molecules of phosphoric acid, $2\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$.

A study of the softening of viscose films (cellophane) with aqueous solutions of glycerol [75] showed that as the concentration of the softening baths increased, the difference between the composition of the solution, held by the film, and the composition of the softening bath decreased and with a softening bath with 65% concentration, this difference disappeared completely, i.e., the film began to absorb the contents of the bath with constant composition. These data on the absorption by a cellulose film of an aqueous glycerol solution of constant composition at a solution concentration of about 65%, at which the glycerol hydrate of composition $\text{C}_3\text{H}_8\text{O}_3 \cdot 3\text{H}_2\text{O}$, found by D. I. Mendeleev in aqueous solutions of glycerol, exists, indicates the significance in absorption of molecular compounds in solution.

Mention should be made of the work of S. N. and N. F. Gintse [74] on the thermal insulation materials of low specific gravity, obtained by mixing cellulose with phosphoric acid and a gas-forming substance. An examination was made of the effect of phosphoric acid concentration, solution time, and solution and precipitation temperature on the volumetric weight and the shrinkage of the mass. Increasing the acid concentration makes it possible to increase the cellulose concentration, which leads to the production of a composition of better forming properties and with a lower specific volume due to an increase in the amount of gas-former, while a very uniform

and fine porosity is obtained. The use of 95-96% phosphoric acid without a frothing agent gives a composition with a volumetric weight of 0.15-0.20, while a cellulose concentration of 8-9% is achieved under laboratory conditions and in work on an experimental apparatus with stone rollers, a cellulose concentration of 11-12% is convenient. All operations were performed at a temperature of about 10°.

One of the most important characteristics of cellulose in the production of cellulose ethers and esters or in the preparation of hydrate fibers is the copper number. The copper number is usually determined under heterogeneous conditions, which is suitable for cellulose fiber, but is not applicable to regenerated, compressed fibers, since under these circumstances the normal method gives low results. S. N. and O. P. Koz'mina [67] developed a method of determining copper numbers under homogeneous conditions in Schweitzer's solution.

Interesting data were obtained on the preparation and study of the properties of modified cellulose molecules, impoverished by one oxygen atom. Investigations were made on developing syntheses and studying the properties of desoxy, anhydro and unsaturated derivatives of cellulose. In joint work with A. A. Lopatenok, S. N. examined conversions of cellulose ethers using the P. P. Shorygin reaction (cleavage with sodium in liquid ammonia) with the aim of preparing desoxy derivatives of cellulose. The best results were obtained with cyanoethyl ethers of cellulose. In the cleavage of cyanoethyl cellulose with sodium in liquid ammonia, the cyanoethyl residues were removed completely, mainly to give hydroxyl groups and partly to give desoxy groups (0.45 groups per glucose residue). In the cleavage of p-toluenesulfonic groups with metallic sodium in liquid ammonia, anhydro derivatives of cellulose were obtained and these could also be obtained by the action of organic bases on p-toluenesulfonic esters of cellulose.

Together with a study of the chemistry of cellulose, the synthesis conditions of cellulose ethers and esters and the mechanism of nitration and transesterification, S. N. made a thorough study of the colloidal chemical properties of cellulose derivatives under processing conditions. Mineral impurities were found to have a great effect on the colloidal chemical properties. In an investigation of acetylcellulose, S. N. et al. [62] established that mineral impurities in acetylcellulose were the reason for the anomalous viscosity and the increased viscosity of its solutions. In contrast to other calcium salts, the presence of calcium acetate in acetylcellulose solution increased the viscosity of acetylcellulose lacquer so much that it could not be determined. To determine the relation between the structural viscosity and the mineral impurity content, investigations were made with dilute solutions to show the effect of structurality, which depends only on the mineral impurities.

S. N. and R. S. Aleksandrova [48] found that for benzylcellulose there was a deviation from the Khagen-Poiseuille law in concentrated solutions and the viscosity was not anomalous in dilute solutions (to 2%). The effect of the solvent on the deviation from Poiseuille's law was established. The viscosity and solubility of ethyl cellulose [46] depended on the nature of the ether, the degree of substitution and the method of treatment and on the viscosity of the liquid components forming the system. It was found that the best solvents, in which clear films with good mechanical and other indexes were obtained, were mixtures of benzene and toluene with alcohol.

In the laboratory of L.T.I. and the Institute of Agrophysics, under the direction of Academician A. F. Ioffe, a large amount of material was obtained on the use of acetylcellulose films instead of glass in hotbeds, since such films will transmit ultraviolet rays well.

In a series of works, a detailed study was made of nitric esters of cellulose and the action of weak and strong bases [43] and acetic acid [76] on nitrocellulose was examined. The reasons for the reduction in the viscosity of nitrocellulose by ammonia was studied [36]. It was shown that in the treatment of nitrocellulose with substances of a basic character, there occurred a partial denitration, accompanied by oxidation of the nitrocellulose, producing fractions, which differed in solubility in alcohol. Such bases as ammonia and pyridine lowered viscosity more strongly than equivalent amounts of strong bases.

In the acetylation of nitrocellulose with acetic acid, it was established that together with the introduction of acetyl groups into the product, there was also a fall in the nitrogen content. Increasing the reaction temperature accelerated the fall in nitrogen, but the total degree of esterification of the cellulose derivatives obtained remained constant. Consequently, the mechanism of the acetylation of nitrocellulose with acetic acid consists of the substitution of nitro groups by acetyl groups.

Like other cellulose esters, nitrocellulose is solvated by solvents and swells in them either to a limited or an unlimited extent. The intensity of the reaction of the solvent with nitrocellulose may be characterized by the swelling pressure. S. N. and M. E. Dyn'kin [70] constructed an original apparatus to determine the swelling pressure

and the work of swelling changed regularly in relation to the nitrogen content of the nitrocellulose and the composition of the solvent, but did not depend on the viscosity of the nitrocellulose. The swelling pressure and the work of swelling made it possible to compare the relative strength of interaction of the different nitrocelluloses with different solvents. With an increase in the degree of nitration, the swelling pressure decreased and there was an increase in the relative and structural viscosities of dilute solutions and in the pressures for squeezing and drying (elimination of solvent from concentrated systems and gels).

An outstanding investigation by S. N. on the mechanism of cellulose nitration confirmed and developed the theory of nitration of Mendeleev and Sapozhnikov. S. N. et al. [68], on the basis of the hydrate theory of Mendeleev and a study of the changes in the physicochemical indexes (vapor pressure, density, electrical conductivity, etc.) with composition of nitration mixtures, established the best conditions for the preparation of highly nitrated nitrocellulose by the action of phosphoric-nitric acid mixtures and showed the determining role of hydration and dehydration of the acids. The swelling of the cellulose is of great importance in the course of nitration. There is a definite linear relation between the degree of nitration and the degree of swelling in mixtures with a low water content. In the case of mixtures with a lot of water or a high nitrogen content swelling is considerable and, with excess nitric acid, the nitration process approaches permutoid reaction*.

The first hydroxybutyl ethers of cellulose were prepared [51] with various degrees of substitution, depending on the reaction conditions, and the maximum degree of substitution was obtained with longer heating times (up to 12 hours) and excess pseudobutylene oxide (up to 10 moles). In contrast to hydroxyethyl ethers of cellulose, which are readily soluble in water, hydroxybutyl ethers of cellulose, even with a high degree of substitution, were difficultly soluble in water due to the complexity of the substituent, but readily soluble in dilute alkali solutions to form extremely viscous solutions. More strongly hydrophilic properties were possessed by glycerol ethers of cellulose, as confirmed by experiment. S. N. et al. [66] obtained new data on the synthesis and the properties of glycerol ethers of cellulose. An examination was made of the action of monochlorohydrin, glycerol epichlorohydrin and glycidic alcohol on alkali cellulose and the effect of impurities on the properties of the glycerol ethers of cellulose obtained was demonstrated. The presence of traces of glycerol dichlorohydrin led to the formation of cross-linked molecules, which sharply changed the solubility of the ethers obtained in hydrophilic solvents. In contrast to the experiments of P. P. Shorygin, S. N. [66] was able to obtain readily soluble glycerol ethers of cellulose after careful purification of glycidic alcohol by repeated distillation.

In the nitration of glycerol ethers of cellulose, obtained using glycerol epichlorohydrin and glycidic alcohol, with nitration mixtures of various compositions, the effect of the nitration mixture composition on the degree of nitration was demonstrated and also the effect of the degree of etherification of the glycerol ethers on the nitrogen content of the nitro product was elucidated. Nitroglycerol ethers of cellulose from glycidic alcohol were considerably more soluble in ketones and esters than ethers obtained through epichlorohydrin.

S. N. Danilov and O. P. Koz'mina [78] studied the oxidative polymerization of allylcellulose and showed that under the action of heat and light, there occurred the addition of oxygen to allyl cellulose with subsequent decomposition of the oxidized molecule at the double bond to eliminate formaldehyde and form a three-membered structure by cross-linking of the ether-cellulose units. Oxidative polymerization also occurred under the action of peroxide compounds. In the absence of oxygen, allyl cellulose was not polymerized. The chlorination of allyl cellulose gave a chloro substituted allyl ether of cellulose, which was readily converted into an unsaturated chloride by the elimination of hydrogen chloride. Under the action of external conditions, the unsaturated chloride in its turn rapidly polymerized to form a chlorine-containing polymer of the chloroprene type.

Among the works of S. N. on the synthesis and study of the properties of hydrophilic ethers of cellulose, is the work on the preparation of carboxymethylcellulose [35]. An examination was made of the synthesis conditions, the effect of alkali concentration and reaction temperature and also the optimal molar ratios of the components, which affect the yield and degree of substitution, were found. Carboxymethylcellulose, which has extremely valuable properties, has found wide application in a series of fields. At the present time carboxymethylcellulose is produced in our factories and widely used in oil-well drilling, as a detergent, as a suspension thickener in printing, etc.

Many ethers of cellulose have been known for a long time, but investigations were not made from the point of view of the chemistry of the interaction of cellulose with alkali in reactions for the preparation of cellulose ethers. The question was whether the reaction proceeded through the alcoholate form or by means of a type of

* Presumably meaning similar to a reaction with permutite - Translator's note.

molecular compound. Using the simple models of plasticizer synthesis (benzyl ethers of ethylene glycol and glycerol), S. N. et al. [41] examined the synthesis of benzyl cellulose and showed that there was complete analogy between the formation of benzyl ethers of cellulose and the etherification of di- and trihydric alcohols, with the exception of the fact that the etherification of cellulose was a heterogeneous process. S. N. developed a rapid method of analyzing benzyl ethers of cellulose for factory control [40]. The method was based on the reduction of the thermal decomposition products of benzyl cellulose at the moment of their formation with hydrogen, formed by reacting aluminum or zinc with solid alkali. The thermal decomposition products of benzyl cellulose, containing the benzoxy group $C_6H_5CH_2O$, were reduced to toluene. This method was also convenient for the analysis of mixed ethers such as ethylbenzyl cellulose and butylbenzyl cellulose.

S. N. made a considerable contribution to the science of natural polymers by his studies on chitin. In contrast to cellulose, chitin swells very little in alkalis and, therefore, will hardly undergo etherification. Conditions were found for activating chitin and under appropriate conditions, it was possible to dissolve chitin in alkali [96]. Glycerol ethers of chitin [97] were prepared for the first time by the action of glycerol monochlorohydrin or glycidic alcohol on alkali chitin. Due to traces of glycerol dichlorohydrin, the alkylation of chitin with glycerol monochlorohydrin gave ethers which did not swell in water and alkali solutions and were even insoluble in concentrated solutions of hydrochloric and phosphoric acids. At the same time, glycerol ethers of chitin, obtained with glycidic alcohol, swelled in water and dissolved in dilute alkali solutions, depending on the degree of substitution. Of other hydrophilic ethers of chitin, the hydroxybutyl ether was prepared for the first time [111]. The optimal conditions were established for the preparation of water- and alkali-soluble ethers, which give viscous solutions in water and dilute acetic acid. There is practical interest in the ethyl ethers of chitin [111], which were prepared for the first time by S. N. and E. A. Plisko. These ethers dissolved in organic solvents forming viscous solutions, from which formed films, which were equal in mechanical properties to ethyl cellulose films. At present, work is proceeding on the preparation of carboxymethyl chitin and the study of its properties, a study is being made of the hydrolysis of chitin and a search is being made for methods of synthesizing other ethers for conversion to unknown anhydro- and desoxychitins.

The work of S. N. Danilov in the field of ethers and esters of cellulose is closely connected with his investigations in the field of cuprammonium solutions of cellulose, xanthates and viscose.

Over many years, S. N. has carried out a large amount of research work on determining the composition, the structure and the properties of cuprammonium compounds of cellulose and the factors affecting the preparation of cuprammonium spinning solutions. In the LTI Laboratory, S. N. investigated the preparation of basic copper salts and copper hydroxide [57], used in the production of cuprammonium fiber; methods for their analysis were developed simultaneously. It was found that, depending on the preparation conditions and the composition of the salts, they differed in the degree of dispersion and solubility in ammonia, which affected the solubility of cellulose and the properties of the spinning solution. Traces of salts, the presence of sulfate ion [58] and the addition of glucose [59] had a great effect on the properties of the solutions. These papers showed the necessity for careful control of the salts' composition in production and strict observation of the preparation conditions.

S. N. was one of the first to propose the method of coagulating a spinning solution by the addition of an electrolyte as a method of rapid control of the readiness of the solution. Under the direction of S. N., a detailed study was made of the effect of electrolytes on the solubility of basic salts and also the action of sulfite salts as agents to raise the viscosity of the solution and protect the cellulose from oxidation [60].

Stable spinning solutions are very difficult to obtain due to the ready oxidizability of the cuprammonium cellulose solution. For a number of years, S. N. has been investigating oxidation processes in cuprammonium cellulose solutions [69]. It was found that the main reason for retardation of oxidation in the presence of organic additives (tartaric acid, mannitol, glycerol, glucose and triethanolamine) was the increased viscosity of the solution due to the formation of compounds with the cuprammonium base by the organic polyhydroxy substances and, as a result, the separation of free copper from the solution. Mineral additives such as sodium sulfite and bisulfite are negative catalysts in the oxidation of cuprammonium solutions of cellulose. Sulfite and cellulose are oxidized very slowly as a conjugated reaction, when both are present in a cuprammonium solution, i.e., the cellulose and sulfite protect each other from oxidation. Here, the sulfite acts as an inhibitor, retarding oxidation [81]. In its turn, cellulose retards sulfite oxidation. Consequently, sulfite behaves not only as a substance which raises the viscosity of the solution and thus prevents it from oxidizing, but also as an agent which destroys the active centers in the substance being oxidized and the active oxygen atoms, thus breaking the oxidation chains at the beginning.

Under S. N.'s direction, extensive work on cuprammonium solutions of cellulose and other polyhydroxy compounds [98] was carried out by various physicochemical methods and this work solved certain problems in the chemistry of these solutions. Experiments with electrophoresis, ion exchange chromatography and spectrometry of the cuprammonium solutions of polyhydroxy compounds refuted the concept of the alcoholate nature of the copper-cellulose compound in the solution.

A direct study of the composition of the precipitates isolated from the cuprammonium solutions of cellulose under the action of salt and alkali solutions [103] indicated the absence from the precipitate of chemical compounds of constant composition, known in the literature as Normann compounds. As a result of these investigations, the cuprammonium solution of cellulose was found to be a molecular solution of a high-molecular substance $\{ (C_6H_{10}O_5)_x \cdot [Cu(NH_3)_m(OH)_2]_y \cdot (H_2O)_z \}_n$, in which the cellulose formed with the cuprammonium base a molecular compound of variable composition, due to hydrogen bonds.

The beginning of S. N. Danilov's work in the field of xanthates and viscoses is connected with the organization in the USSR of the viscose artificial fiber industry. Many of S. N.'s works of this period are directly connected with problems of industrial technology. During these years S. N. wrote detailed reviews on the most important achievements of the time in the chemistry of xanthates, viscose and artificial fibers [115-117, 123]. It was then that the main directions of S. N.'s further experimental investigations in this field took shape.

The main series of works by S. N. on the chemistry of xanthates and viscose was devoted to a study of the chemical reactions of cellulose xanthates, viscose composition, in particular, the polysulfide compounds in viscose that had been unknown previously, the role of separate components of viscose and additives, the complex processes of viscose ripening and the problem of carbon disulfide distribution in the main and side reactions in cellulose xanthation. S. N. and his co-workers found new data on the composition of viscose and its ripening process, which resulted in the creation of a special section on the chemistry of viscose and in the formulation of new views on the processes occurring in viscose.

S. N. was the first to put forward the hypothesis that in the ripening of viscose, besides the hydrolytic processes, oxidation reactions also occur. It follows from S. N.'s work that in viscose solutions of cellulose there are, so to speak, model reactions of organic oxygen- and sulfur-containing substances, so that the oxidation in viscose may be divided into two large categories: 1) oxidation processes involving atmospheric oxygen, which affects the cellulose and other components of viscose solutions, and 2) oxidation and oxidation-reduction reactions of the sulfur-containing compounds in the viscose, which are capable of oxidation or donation and addition of sulfur [81]. The main works of S. N. on the chemistry of xanthates and viscose are devoted to the study of these two directions. Schemes for the oxidation reactions in viscose, proposed by S. N., are given in monographs and text books, describing the ripening processes of viscose.

Since 1934, the study of polysulfide compounds in viscose and their role in oxidation-reduction reactions is developed in S. N.'s work. The thioanhydride of cellulose xanthic acid was prepared for the first time by treating cellulose xanthate with benzoyl chloride [44]. Later on, first using models of simpler compounds (derivatives of ethyl ether, menthol and diacetoneglucose) and then using cellulose derivatives, it was shown that dixanthates were converted to thioanhydrides by the action of sulfur acceptors such as cyanides and sodium sulfide and sulfite [77, 85, 86]. The reactions of dixanthates of simple compounds (ethyl alcohol and the monobenzyl ether of ethylene glycol) and cellulose, when treated with sodium hydroxide and aniline, were studied in detail [72]. It was established that cellulose dixanthates do not differ in structure from the dixanthates of simple alcohols, which was questioned at one time by some authors (Berl' and Dilenius and Geiger). * It was shown [84] that during the oxidation of cellulose xanthate with oxygen, cellulose dixanthate was formed. Cellulose dixanthate was shown to be formed in viscose [84] under the action of atmospheric oxygen. It was established that the formation of dixanthates in viscose and their subsequent, inevitable decomposition in a strongly alkaline medium with the formation of xanthate with a lower degree of substitution and the accumulation of side products in the viscose [72], must accelerate the ripening of viscose. A study of the properties of thioanhydrides of cellulosexanthic acid [86] showed that due to the instability of the thioanhydride in alkali, it could not exist in viscose, although one cannot exclude the possibility of its formation in the ripening of viscose from cellulose dixanthate under the action of sulfur-abstracting substances, contained in viscose (sodium sulfide and sulfite). It was established that the side products in viscose included polysulfide compounds, such as sodium disulfide and perthiocarbonate, in addition to thiosulfate, which was known previously. This was proved both by indirect reactions with cyanide [55] and in subsequent investigations of viscose spectrographically. It was proved that polysulfide compounds accumulate in viscose as it ripens [85]. The mechanism of the action of sulfite in viscose, producing a more advantageous distribution of carbon disulfide, was elucidated [55].

* Transliteration of Russian - Publisher's note.

Parallel with the study of the oxidative processes in viscose, a detailed study was made of the oxidative reactions and their inhibitors in alkali cellulose. This investigation was a most convenient example for a study of oxidative conversions of cellulose [84].

In papers devoted to elucidating the role of different components of viscose and its conversions, a study was made of the action of atmospheric oxygen, sulfur-abstracting substances and oxidation inhibitors on pure preparations of these components [84, 85]; the effect of alkali and salts on the decomposition rate of the xanthates of viscose was found [108]. An examination was made of the interaction of viscose components and the formation of sodium sulfide, as the initial substance forming trithiocarbonate, was noted.

During the investigations, S. N. and his co-workers developed new procedures and methods of analysis, including: the determination of the free carbon disulfide in viscose and xanthate [56], the determination of the degree of xanthation by means of chloroacetonitrile derivatives [67], analysis of viscose components in the form of cadmium [56] or zinc [108] salts, fractionation of xanthates with salt solutions [55] and the determination of polysulfide compounds by the cyanide method [85] in various ways, including the use of potentiometric titration. Tracer methods were used to determine the distribution of carbon disulfide in viscose between the components and to determine the sulfur donation of polysulfide compounds for the first time. See page 3221.

As has already been said, in a series of works, S. N. developed aspects—closely related to the technology of viscose production. In answer to the industrial problems in the development of the technology of producing viscose continuously, a study was made of the effect of various factors of the first stage of the process—mercerization—(increasing the temperature and changing the ratio of cellulose and alkali in the alkali cellulose) on the distribution of carbon disulfide in the xanthation between the main product (xanthate) and the side reactions [42]. Recently, it was shown to be possible to carry out a rapid emulsion xanthation with the production of a viscose with industrial characteristics. This xanthation was performed both with direct and reverse emulsions of carbon disulfide. The emulsions were obtained by the action of ultrasonics or by the use of the preparation OP-10 as an emulsifier [113].

As industry required an artificial fiber which could be dyed with wool dyes, a method was developed for rendering viscose wool-like with wool hydrolyzate. A series of works were carried out on the selection of the composition of precipitating baths. The physicochemical characteristics of the baths were described and it was shown that determination of the electroconductivity of the baths served as a good characteristic and indicated changes in the ionic balance during spinning [47]. The action of different salts on the decomposition and coagulation of viscose by baths was compared by an original method for separately studying the decomposing and coagulating action of baths [47, 61, 63] and equivalence coefficients were found for the main salt components of precipitating baths in relation to the slowing of the decomposing and the increase in the coagulating action of the baths [61]. The coefficients found were tested under actual conditions of spinning in a study on the action of various precipitating baths by an analysis of the filaments formed [63]. This showed the possibility of an efficient choice of the composition of precipitating baths on the basis of calculations and considerably extended previous attempts in this direction. A study was made of the conversions of sugars (hexoses and pentoses) in precipitating baths [53] and this was of particular interest as, in addition to the accumulation of hydrolysis products of the polysaccharides from the spun filaments in the bath, glucose was specially introduced into the baths for its softening effect, according to accepted recipes. The use of monosaccharides in the baths was shown to be unprofitable as the accumulation of sugars in the bath lead to the formation of gummy, lignin-like substances, which could produced inhomogeneous coloring of the fibers in textile treatment. The introduction of monohydric alcohols or hydroxyacids into the bath instead of monosaccharides was proposed.

Considerable work was done on the purification of exhausted alkalis from organic impurities with oxidizing agents [54], which have an effect on the practical purification of alkalis. A detailed investigation was made in laboratory experiments and on an experimental apparatus on the regeneration of products, emitted with factory flue gas, and also the problem of viscose production [64, 65]. Many valuable practical directions for the technology of viscose production were provided by the work of S. N. at LTI in cooperation with industry and presented in numerous reports.

This is a far-from-complete account of the problems and subjects which were and are being worked out under the direction of S. N. Danilov by his numerous students and colleagues, both in the field of the theoretical foundations of cellulose chemistry and in the field of the practical application of cellulose and its derivatives, as well as other high-molecular compounds.

LITERATURE CITED

- [1] S. N. Danilov, J. Russ. Chem. Soc. 49, 282 (1917).
- [2] S. N. Danilov, J. Russ. Chem. Soc. 50, 296 (1918).
- [3] S. N. Danilov, J. Russ. Chem. Soc. 51, 97 (1919).
- [4] S. N. Danilov, J. Russ. Chem. Soc. 51, 128 (1919).
- [5] S. N. Danilov, J. Russ. Chem. Soc. 51, 133 (1919).
- [6] S. N. Danilov, J. Russ. Chem. Soc. 52, 369 (1920).
- [7] S. N. Danilov, J. Russ. Chem. Soc. 52, 400 (1920).
- [8] S. N. Danilov and E. D. Venus-Danilova, J. Russ. Chem. Soc. 57, 347 (1925).
- [9] S. N. Danilov and E. Venus-Danilova, J. Russ. Chem. Soc. 57, 428 (1925).
- [10] S. N. Danilov, Coll. Trans. State Inst. Appl. Chem. 5, 66 (1926).
- [11] E. D. Venus-Danilova and S. N. Danilov, J. Russ. Chem. Soc. 58 (1926).
- [12] S. N. Danilov, J. Russ. Chem. Soc. 58, 129 (1926).
- [13] S. N. Danilov, J. Russ. Chem. Soc. 58, 148 (1926).
- [14] S. N. Danilov and E. Venus-Danilova, J. Russ. Chem. Soc. 58, 957 (1926).
- [15] S. Danilov and E. Venus-Danilova, Ber. 59, 377 (1926).
- [16] S. Danilov and E. Venus-Danilova, Ber. 59, 1032 (1926).
- [17] E. D. Venus-Danilova and S. N. Danilov, J. Russ. Chem. Soc. 59, 22 (1927).
- [18] S. N. Danilov and E. Venus-Danilova, J. Russ. Chem. Soc. 59, 187 (1927).
- [19] S. Danilov and E. Venus-Danilova, Ber. 60, 1050 (1927).
- [20] S. N. Danilov, J. Russ. Chem. Soc. 59, 1105 (1927).
- [21] S. N. Danilov, J. Russ. Chem. Soc. 59, 39 (1927).
- [22] S. Danilov, Ber. 60, 2390 (1927).
- [23] S. N. Danilov and E. Venus-Danilova, J. Russ. Chem. Soc. 61, 1661 (1929).
- [24] S. N. Danilov, J. Russ. Chem. Soc. 61, 723 (1929).
- [25] S. Danilov and E. Venus-Danilova, Ber. 62, 2653 (1929).
- [26] S. N. Danilov, E. D. Venus-Danilova and P. S. Shantarovich, J. Russ. Chem. Soc. 62, 494 (1930).
- [27] S. N. Danilov, E. Venus-Danilova and P. Shantarovich, J. Russ. Chem. Soc. 62, 1377 (1930).
- [28] S. Danilov, E. Venus-Danilova and P. Schantarovitsch, Ber. 65, 2269 (1932).
- [29] S. N. Danilov and E. Venus-Danilova, J. Russ. Chem. Soc. 62, 1697 (1930).
- [30] S. Danilov and E. Venus-Danilova, Ber. 63, 2765 (1930).
- [31] S. N. Danilov, V. Driakhlitsyna and O. Manokhina, J. Gen. Chem. 1, 515 (1931).
- [32] S. N. Danilov and A. Meos and Deich, Ref. Coll. Synth. Fibers Sci. Res. Inst. (1936).
- [33] E. D. Venus-Danilova and S. N. Danilov, J. Gen. Chem. 2, 645 (1932).
- [34] S. N. Danilov and E. D. Venus-Danilova, J. Gen. Chem. 3, 559 (1933).
- [35] S. N. Danilov and N. Krestinskaia, Plastics, No. 4 (1933).

- [36] S. N. Danilov, *Artificial Fibers*, No. 8 (1933).
- [37] S. N. Danilov and R. Sviridovskaya, *The Oil and Fat Business*, No. 6, 5 (1933).
- [38] S. Danilov and E. Venus-Danilova, *Ber.* 67, 24 (1934).
- [39] S. N. Danilov, L. Kremnev and P. Petukhov, *Artificial Fibers*, No. 1, 19 (1934).
- [40] S. N. Danilov and A. Iokhel', *Plastics*, No. 1, 33 (1934).
- [41] S. N. Danilov, *Plastics*, No. 2, 11 (1934).
- [42] S. N. Danilov and S. Rozov, *Artificial Fibers*, No. 2, 16 (1954).
- [43] S. N. Danilov, *J. Gen. Chem.* 4, 817 (1934).
- [44] S. N. Danilov and D. S. Brokhina, *J. Gen. Chem.* 4, 995 (1934).
- [45] S. Danilov, *Ber.* 67, 264 (1934).
- [46] S. N. Danilov and R. S. Aleksandrova, *Coll. "Plastics,"* 100 (1935).
- [47] S. N. Danilov and L. F. Rogulev, *Artificial Fibers*, No. 4, 241 (1935).
- [48] S. N. Danilov and R. S. Aleksandrova, *Plastics*, No. 4, 23 (1935).
- [49] S. N. Danilov and S. M. Rizov, *J. Gen. Chem.* 5, 1696 (1935).
- [50] S. N. Danilov and A. M. Gakhokidze, *J. Gen. Chem.* 6, 704 (1936).
- [51] S. N. Danilov and V. A. Kon'kova, *J. Appl. Chem.* 9, 1863 (1936).
- [52] S. Danilov and A. Gachokidze, *Ber.* 69, 2130 (1936).
- [53] S. N. Danilov, E. V. Zaitseva and L. A. Tsaplina, *Ind. Org. Chem.* No. 11, 395 (1936).
- [54] S. N. Danilov and I. P. Sukhovtseva, *Ind. Org. Chem.* No. 21, 648 (1936).
- [55] S. N. Danilov and S. M. Rizov, *Ind. Org. Chem.* No. 12, 696 (1937).
- [56] S. N. Danilov and S. M. Rizov, *J. Appl. Chem.* 10, 1045 (1937).
- [57] S. N. Danilov, A. Cherniaeva, N. Goriunova and Iu. Gol'dfarb, *J. Appl. Chem.* 10, 1598 (1937).
- [58] S. N. Danilov, Iu. Gol'dfarb, A. Cherniaeva and Goriunova, *J. Appl. Chem.* 10, 1457 (1937).
- [59] S. N. Danilov, D. Brokhina and E. Martynova, *J. Appl. Chem.* 10, 1615 (1937).
- [60] S. N. Danilov and E. P. Chilina, *J. Appl. Chem.* 11, 1522 (1938).
- [61] S. N. Danilov and N. F. Gintse, *Ind. Org. Chem.* No. 12, 736 (1938).
- [62] S. N. Danilov, Iu. Gol'dfarb and E. Zaitseva, *J. Appl. Chem.* No. 9, 511 (1939).
- [63] A. N. Gintse, O. Plushch and I. Samarskii, *Ind. Org. Chem.* No. 9, 511 (1939).
- [64] S. N. Danilov, *Ind. Org. Chem.* No. 12, 674 (1939).
- [65] S. N. Danilov and V. Kon'kova, *Plastics*, No. 3, 50 (1939).
- [66] S. Danilov, M. Dyn'kin and students Orlova and Rabiniaev, *J. Gen. Chem.* 9, 1674 (1939).
- [67] S. N. Danilov, *Trans. All-Union Conf. on Anal. Chem.* 3, 204 (1944).
- [68] S. N. Danilov, V. M. Matveev and V. I. Bukhgalter, *J. Gen. Chem.* 10, 527 (1940).
- [69] S. N. Danilov and A. Kozakevich, *J. Appl. Chem.* 13, 1667 (1940).
- [70] S. N. Danilov and M. E. Dyn'kin, *J. Gen. Chem.* 15, 550 (1945).
- [71] S. N. Danilov and P. T. Pastukhov, *J. Gen. Chem.* 16, 923 (1946).

- [72] S. N. Danilov and O. P. Koz'mina, J. Appl. Chem. 19, 1059 (1946).
- [73] S. N. Danilov and P. T. Pastukhov, J. Gen. Chem. 17, 1140 (1947).
- [74] S. N. Danilov and N. F. Gintse, Authors Cert. No. 66331 from May 31, 1946.
- [75] S. N. Danilov, M. A. Sokolovskii and A. I. Evdokimova, J. Gen. Chem. 17, 507 (1947).
- [76] S. N. Danilov, M. A. Sokolovskii and A. I. Evdokimova, J. Gen. Chem. 17, 1888 (1947).
- [77] S. N. Danilov and N. M. Grad, J. Gen. Chem. 17, 2193 (1947).
- [78] S. N. Danilov and O. P. Koz'mina, J. Gen. Chem. 18, 1823 (1948).
- [79] S. N. Danilov and N. S. Tikhomirova, J. Gen. Chem. 18, 1956 (1948).
- [80] S. N. Danilov, J. Gen. Chem. 18, 2000 (1948).
- [81] S. N. Danilov, Trans. IV Conf. on High-Molecular Compounds, 63 (1948).
- [82] S. N. Danilov, Trans. IV Conf. on High-Molecular Compounds 88 (1948).
- [83] S. N. Danilov and O. P. Koz'mina, J. Gen. Chem. 19, 309 (1949).*
- [84] S. N. Danilov, N. M. Grad and E. I. Geine, J. Gen. Chem. 19, 826 (1949).*
- [85] S. N. Danilov, N. M. Grad and A. F. Vorob'eva, J. Gen. Chem. 19, 1257 (1949).*
- [86] S. N. Danilov, N. M. Grad and V. O. Klesman, J. Appl. Chem. 22, 625 (1949).
- [87] S. N. Danilov, Trans. Conf. on Catalysis, 309 (1949).
- [88] S. N. Danilov and I. S. Lishanskii, Authors Cert. No. 89,985 from November 3, 1950.
- [89] S. N. Danilov and I. S. Lishanskii, J. Gen. Chem. 21, 366 (1951).*
- [90] S. N. Danilov and V. F. Martynov, J. Gen. Chem. 22, 1572 (1952).*
- [91] S. N. Danilov and K. A. Ogloblin, J. Gen. Chem. 22, 2113 (1952).*
- [92] S. N. Danilov and V. F. Kazimirova, J. Gen. Chem. 23, Coll. II, 1646 (1953).*
- [93] S. N. Danilov, Coll. Problems in the Mechanism of Organic Reactions, Kiev, 1954, 247.
- [94] S. N. Danilov and N. S. Tikhomirova-Sidorova, J. Gen. Chem. 24, 458 (1954).*
- [95] S. N. Danilov and N. S. Tikhomirova-Sidorova, J. Gen. Chem. 24, 455 (1954).*
- [96] S. N. Danilov and E. A. Plisko, J. Gen. Chem. 24, 1761 (1954).*
- [97] S. N. Danilov and E. A. Plisko, J. Gen. Chem. 24, 2071 (1954).*
- [98] S. N. Danilov and M. G. Okun', J. Gen. Chem. 24, 2153 (1954).*
- [99] S. N. Danilov and L. I. Rastorgueva, J. Gen. Chem. 25, 1590 (1955).*
- [100] S. N. Danilov and I. S. Lishanskii, J. Gen. Chem. 25, 2106 (1955).*
- [101] S. N. Danilov, Memoria 28 congreso internacional de quimica industrial 2, 990 (1955).
- [102] S. N. Danilov, Coll. Reactions and Methods of Investigation of Organic Compounds, Vol. IV, Moscow, 159 (1956).
- [103] S. N. Danilov and M. G. Okun', J. Gen. Chem. 26, 3005 (1956).*
- [104] S. N. Danilov and N. F. Gintse, J. Gen. Chem. 26, 3014 (1956).*
- [105] S. N. Danilov, O. P. Koz'mina and L. N. Shirshova, J. Gen. Chem. 27, 945 (1957).*
- [106] S. N. Danilov and V. I. Ivashchenko, J. Gen. Chem. 27, 2093 (1957).*
- [107] S. N. Danilov, A. N. Anikeeva, N. S. Tikhomirova-Sidorova and A. N. Shirshova, J. Gen. Chem. 27, 2434 (1957).*

*Original Russian pagination. See C. B. Translation.

- [108] S. N. Danilov and H. F. Gintse, *J. Gen. Chem.*, 27, 3290 (1957).*
- [109] M. F. Ishanina, Iu. A. Stepanov and S. N. Danilov, *Trans. LTI*, 42, 16 (1957).
- [110] M. F. Ishanina, Iu. A. Stepanov and S. N. Danilov, *Trans. LTI*, 42, 30 (1957).
- [111] S. N. Danilov and E. A. Plisko, *J. Gen. Chem.*, 28, 2217 (1958).*
- [112] S. N. Danilov, Thesis of Reports to the Conference on Chemistry and Carbohydrate Metabolism in Animal and Plant Organisms, Moscow, 6 (1958).
- [113] S. N. Danilov, N. S. Tikhomirova-Sidorova and O. M. Kulakova, *J. Appl. Chem.*, 31, 765 (1958). *
- [114] S. N. Danilov, *Nature*, No. 11-12, 1039 (1932).
- [115] S. N. Danilov, *The Lacquer and Paint Industry*, 2, 25 (1933).
- [116] S. N. Danilov, in the book of V. Vel'tsina, "The Chemistry and Physics of Artificial Fiber Technology, State Chem. Tech. Inst. 531 (1933).* *
- [117] S. N. Danilov, *Synthetic Fibers Sci. Res. Inst. Coll.* 1, 5 (1934).
- [118] S. N. Danilov, *Nature*, No. 6, 91 (1934).
- [119] S. N. Danilov, *Nature*, No. 11, 74 (1934).
- [120] Iu. S. Zal'kind and S. N. Danilov, *J. Gen. Chem.*, 4, 733 (1934).
- [121] S. N. Danilov, in the book of A. E. Favorskii, *Selected Works* (1934).* *
- [122] S. N. Danilov, in the book by A. E. Favorskii, *Selected Works* (1940).* *
- [123] S. N. Danilov, *J. Gen. Chem.*, 10, 387 (1940).
- [124] S. N. Danilov, *Prog. Chem.* No. 6 (1945).
- [125] S. N. Danilov and E. D. Venus-Danilova, *Bull. LTI*, No. 12 (1946).
- [126] S. N. Danilov, *Bull. LSU*, No. 1, 103 (1947).
- [127] S. N. Danilov, *Nature*, No. 9, 103 (1936).
- [128] S. N. Danilov, *J. Gen. Chem.*, 18, 1 (1948).
- [129] S. N. Danilov, *J. Gen. Chem.*, 20, 2302 (1950).*
- [130] S. N. Danilov, *J. Gen. Chem.*, 21, 1733 (1951).*
- [131] S. N. Danilov, Newspaper "The Technologist" of January 25, 1952.
- [132] S. N. Danilov, *J. Gen. Chem.*, 23, 160 (1953). *
- [133] S. N. Danilov, *The Frontier of Science and Techniques*, No. 1, 69 (1935).
- [134] S. N. Danilov, *Nature*, No. 9 (1937).
- [135] S. N. Danilov, *J. Appl. Chem.*, 15, 396 (1942).
- [136] S. N. Danilov, *Coll. Soviet Chemistry over 25 Years*, Acad. Sci. USSR Press (1942).* *
- [137] S. N. Danilov, *Coll. The 30th Anniversary of the October Revolution*, Acad. Sci. USSR Press, 582 (1947).* *
- [138] S. N. Danilov, *J. Gen. Chem.*, 17, 1925 (1947).
- [139] S. N. Danilov, *Bull. LSU*, No. 12, 93 (1952).
- [140] S. N. Danilov, *Nature*, No. 10, 17 (1934).
- [141] S. N. Danilov, *Nature*, No. 10, 17 (1934).

*Original Russian pagination. See C. B. Translation.

* * In Russian.

ANHYDRO, DESOXY AND UNSATURATED DERIVATIVES OF POLYSACCHARIDES

I. DESOXYCELLULOSE FROM CYANOETHOXYLCELLULOSE

S. N. Danilov and A. A. Lopatenok

Desoxidated monosaccharide derivatives, containing methylene groups instead of secondary alcohol groups (desoses) and methyl groups instead of primary alcohol groups (methyloses), occur in nature and may be synthesized by several methods. There are a few papers available on the preparation of desoxidated cellulose with the composition $(C_6H_{10}O_5-x)_n$, largely containing methyl groups and synthesized successively through the tosyl esters and iodo derivatives, mainly at the expense of primary alcohol groups.

Moreover, desoxidated celluloses were prepared by reduction [1, 2] either of iodo derivatives $(C_6H_{10-x}O_5-xI)_n$ directly or of unsaturated compounds (celluloseens), formed from iodo derivatives by elimination of hydrogen iodide.

A general method of preparing desoxidated celluloses with methylene and methyl groups was proposed by P. P. Shorygin on the basis of his reaction [3] of cleaving ethers with sodium alkyls [3] or metallic sodium [4], in particular in liquid ammonia.

Alkali metals in liquid ammonia remove acetyl groups from acetyl derivatives of sugars, forming alcoholates of the sugars [5, 6]. In the works of P. P. Shorygin and N. N. Makarova-Zemlianskaia (N. N. Shorygina), the cleavage of ethers with sodium in liquid ammonia was applied to methylated sugars [7, 8] and also to methyl cellulose [9], the benzyl ether of cellulose and acetylcellulose.

Desoxidation of cellulose was achieved in the case of methyl cellulose.

About 15% of the methoxyl groups, available in the methyl cellulose, were cleaved in the direction of desoxycellulose formation through the metalloorganic compound, 25% in the direction of alkali cellulose formation and organometallic alkyl compounds and about 50% of the methoxyls were completely unaffected. Thus partially desoxidated methyl celluloses were obtained. We treated [10] industrial ethyl cellulose (46.8% OC_2H_5 , degree of substitution 2.4) with sodium in liquid ammonia.

Partial cleavage of the ethoxyls with the formation of desoxy groups was observed and a corresponding amount of ethyl alcohol was isolated from the reaction mixture. The product obtained was shown to contain a small amount of methyl groups instead of primary alcohol groups by the formation of methylfurfural during decomposition of the product with 12% hydrochloric acid. However, it was impossible to attain a considerable cleavage of ethoxyl groups of ethyl cellulose by the action of sodium in liquid ammonia.

Considering the fact that the action of acrylonitrile on cellulose in the presence of alkali gives cyanoethoxyl ethers of cellulose, while the reverse cleavage of acrylonitrile from cyanoethoxylcellulose is possible in the presence of alkali, one would expect the more ready cleavage of cyanoethoxyl groups. We performed the experiments described below on the desoxidation of this ether of cellulose (I) by the action of sodium in liquid ammonia.

As these experiments showed, cyanoethoxylcellulose was partly desoxidated in this way, but the direct cleavage of acrylonitrile mainly occurred. We isolated desoxycellulose (II), free from ether groups. There was no noticeable formation of carboxyethylcellulose $[C_6H_{10-x}O_5-x(OCH_2CH_2COOH)]_n$, as is possible if the nitrile groups of the original ether are hydrolyzed [11], but the reaction products did contain acrylic acid (IV) and polyacrylonitrile (V). The acrylic acid may be obtained through β -hydroxypropionic acid (III).



sulfuric acid they did not leave sodium sulfate. This proved that the product did not contain carboxyl groups, which could have been formed by hydrolysis of the nitrile groups.

Synthesis of desoxycelluloses and their properties. For the preparation of desoxycellulose, an apparatus was set up, consisting usually of a wide reaction tube, placed in a Dewar vessel for cooling (with solid carbon dioxide and acetone) and fitted with a gas inlet tube going to the bottom for the admission of ammonia, a funnel (with a stopper) for the introduction of solid reaction components and an outlet tube up through the stopper for the outlet of gases, which were then absorbed in receivers. Gaseous ammonia from a tank was lead through a flowmeter into drying columns (solid sodium hydroxide and soda lime) and the air was flushed from the apparatus with dry ammonia. The dried cellulose ether was first dissolved in liquid ammonia (pale pink solution) and then sodium introduced in small pieces, when a blue solution was obtained. The reaction was performed at the temperature of the cooling mixture and in some cases, at the boiling point of liquid ammonia. The solution was stirred by the passage of the ammonia stream. In some experiments the reaction was performed in a three-necked flask, fitted with a stirrer (stirring for 2-5 hours) for more vigorous stirring. When the components had reacted, the

TABLE

Properties of Original Cellulose Ethers and Desoxycellulose

Name of compound	Found (in %)				Formula of a unit of the compound (calculated)
	C	H	N	CH ₂ COOH or NO ₂ & degree of substitution	
Cyanoethoxycellulose (I)	—	—	8.81	—	C ₆ H ₇ O ₂ (OH) _{1.46} (OCH ₂ CH ₂ CN) _{1.54}
Desoxycellulose (II)	46.4	6.45	—	—	C ₆ H ₇ O ₂ H _{0.45} (OH) _{2.55}
Acetyldesoxycellulose (IV)	49.29	6.35	—	47.2/2.6	C ₆ H ₇ O ₂ H _{0.45} (OCOCH ₃) _{2.55}
Nitrodesoxycellulose (VII)	—	—	—	13.2/2.6	C ₆ H ₇ O ₂ H _{0.45} (ONO ₂) _{2.55}

reaction vessel was removed from the cooling mixture and the ammonia removed through a tube with soda lime. Then moist ether was carefully added to decompose the metalloorganic compounds and then methyl alcohol to destroy the unreacted sodium. The alcoholate was then decomposed with water. It was not advantageous to change this order of introducing the reaction components, i.e., to add the fibrous cellulose ether to a solution of sodium in ammonia, as, in this case, acrylonitrile polymer was deposited on the fiber, hindering the reaction.

300 ml of liquid ammonia was condensed onto 10 g of cyanoethoxycellulose (degree of substitution 1.54) and 5 g of sodium introduced.

In a series of experiments, we established the effect on the course of the cleavage of cyanoethoxyl groups of: 1) the concentration of cellulose ether and sodium in the solution, which are of particular importance, and 2) the reaction time. Under homogeneous reaction conditions, it was necessary to treat the cellulose ether for about 12 hours with 20-24 g-atoms of sodium per glucose residue (about 6 atoms per hydroxyl) and up to 100 ml of liquid ammonia per g of cellulose ether.

If the product still contained nitrogen after the first treatment, a second treatment was necessary and this proceeded under heterogeneous conditions due to the insolubility of desoxycellulose in ammonia. The product was washed and dried after the first treatment and retarded with 6 atoms of sodium per ether group at the boiling point of ammonia for 6 hours. Careful stirring was necessary. The cellulose chains were not disrupted, even after many treatments; the yields of product were good. After removal of the ammonia, it was necessary to add moist ether and then alcohol to the vessel to decompose sodioorganic compounds and to convert the sodium into alcoholate, otherwise, an explosion could occur. The wash liquids were collected to examine the nature of the side products (acrylic acid, etc). The desoxycellulose obtained was acetylated by the usual method with a mixture of acetic anhydride and acetic acid (1:1) with a catalyst (perchloric acid) in a ratio of 1:14 for 24 hours. The

product was insoluble in the acetylation mixture in contrast to normal acetylcellulose. The acetylation product was isolated and prepared for analysis in the usual way. A second acetylation did not change the acetylation product. The acetyl number or else the acetic acid content corresponded to the composition found for the desoxycellulose, which was acetylated. The same desoxycellulose samples were nitrated with nitric acid in methylene chloride. The nitro product also corresponded to the composition of desoxycellulose, in which 0.45 out of the three hydroxyls had been reduced. Comparison of the original ether of the desoxidated cellulose and its acetate and nitrate (see Table) confirmed that partially desoxidated cellulose had actually been obtained from the cyanoethoxycellulose.

The desoxycellulose was analyzed for methyl-group content by hydrolysis with 12% hydrochloric acid; this gave an amount of the phloroglucide of methylfurfural corresponding to 3.4% of methylpentosans or 0.04 desoxy groups for every 3 hydroxyls in the cellulose unit; consequently, there were about 0.4 methylene groups per glucose unit in the desoxycellulose. Available data on the fact that in the synthesis of cellulose ethers the secondary hydroxyls are predominantly etherified, give grounds for thinking that in cyanoethoxycellulose, the ether groups are mainly at positions 2 and 3 and that they are partially desoxidated, but this requires proof.

Some confirmation of the course of the desoxidation reaction is provided by the fact that the reaction products contained only one product - acrylic acid. We could not detect either propionitrile or propionic acid, which could have been formed had the group been eliminated as the sodioorganic compound (formulas VIII and IX). Ethylene cyanohydrin and hydracrylic acid were not detected, probably due to dehydration of the hydracrylic acid.

When the desoxycellulose had been filtered from the reaction mixture, the residual alkaline aqueous ether-alcohol liquid was acidified and acrylic acid isolated, as proved by rapid bromination and analysis of the lead salt.

Found %: Pb 58.8. Calculated %: Pb for the acrylic acid salt 59.3%. Propionic acid was not found.

SUMMARY

1. When treated with metallic sodium, cyanoethoxycellulose completely loses the cyanoethoxyl groups, partly in the form of acrylic (hypothetically, hydracrylic) acid, to form methylene groups and partly methyl groups in the glucose units instead of alcohol groups, i.e., to form desoxycellulose.

Part of the cyanoethoxyl groups are eliminated with the formation of desoxy groups and the other part in the form of acrylonitrile due to the reversal of cyanoethylation in an alkaline medium.

2. The presence of desoxy groups in the product was confirmed by analyses of the product obtained and its acetate and nitrate.

LITERATURE CITED

- [1] F. Cramer and C. Purves, *J. Am. Chem.* 61, 3458 (1939).
- [2] E. D. Kaverzneva, V. I. Ivanov and A. S. Salova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 369 (1949).
- [3] P. P. Shorygin, *Ber.* 43, 1931 (1910); 57, 1627 (1924).
- [4] P. P. Shorygin and S. A. Skoblinskaia, *Proc. Acad. Sci. USSR* 14, 505 (1937).
- [5] Irwing and Muscat, *J. Am. Chem. Soc.* 56, 639 (1934).
- [6] Schmid, *Ber.* 58, 1966 (1925); *Monatsh.* 49, 107 (1928).
- [7] P. P. Shorygin and N. N. Makarova-Zemlianskaia, *Proc. Acad. Sci. USSR* 23, 908 (1939).
- [8] N. N. Shorygina, *J. Gen. Chem.* 19, 1101 (1949);* *Trans. of Conf. on High-Molecular Compounds*, 30 (1945).**
- [9] P. P. Shorygin and N. N. Makarova-Zemlianskaia, *Proc. Acad. Sci. USSR* 14, 509 (1937).
- [10] A. A. Lopatenok, *Syntheses of Desoxycelluloses, Anhydrocelluloses and Celluloseens and a Study of Their Properties*, Diss. Leningrad Tech. Inst. Leningrad (1953).**

*Original Russian pagination. See C. B. Translation.

**In Russian.

- [11] Z. A. Rogovin and A. G. Iashunskaja, Authors Certificate 77, 409 (1949).
- [12] F. Gardner, J. Polym. Sci. 1, 289 (1946).
- [13] J. Mac Gregor, J. Soc. Dyers Colourists, 2, 66 (1951).

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ANHYDRO, DESOXY AND UNSATURATED DERIVATIVES OF POLYSACCHARIDES

II. THE SYNTHESIS OF ANHYDROCELLULOSE FROM p-TOLUENESULFONIC ESTERS

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Anhydro derivatives of monosaccharides and polyhydric alcohols are known with various sizes and positions of the oxide rings.

In a series of cases, the anhydrides of monosaccharides, especially with 3,6-, 5,6- and 2,3-rings, are synthesized through the p-toluenesulfonic (tosyl) esters and sometimes through halogen derivatives of the monosaccharides by the action of alkaline agents [1].

There is only one paper [2] in which there is a description of the preparation of anhydrocellulose in the form of the mixed tosyl and acetic esters from the mixed tosyl and acetic ester of cellulose by the action of 1 N sodium hydroxide solution in methyl alcohol.

To synthesize anhydrocellulose, whose composition may be represented by the general formula $(C_6H_{10-2x}O_{5-x})_n$, tosyl esters of cellulose $[C_6H_{10-x}O_{5-x}(OSO_2C_6H_4CH_3)_x]_n$ of various degrees of esterification were treated with sodium in liquid ammonia or with organic bases (piperidine, etc) [3].

The use of piperidine for the elimination of p-toluenesulfonic acid gave cellulose derivatives, evidently of an anhydride nature, containing chemically bound piperidine and partly unremoved tosyl groups, which complicated the characteristics of the substances obtained [4].

Below, samples of anhydrocellulose are described, which were prepared by the action of sodium in liquid ammonia on tosylcellulose and whose composition was confirmed by analysis of them and their acetates. It is clear that the removal of tosyl groups may proceed 1) with the formation of anhydro rings or 2) as a result of hydrolysis, which is inevitable in the case of highly tosylated esters.

Since tosyl groups in cellulose are predominantly on primary alcohol groups [5], partially on secondary alcohol groups and very slightly on tertiary alcohol groups, it can be postulated that in our samples of anhydrocellulose, the anhydro rings were between the 6th and 2nd or 3rd atoms of the glucose unit, between the 5th and 6th atoms and, to a lesser extent, between the 2nd and 3rd atoms. In the latter case one would expect transposition [1] of the hydrogen atom and the hydroxyl group at the second and third alcohol groups of the glucose unit of the cellulose molecule (Walden inversion). The problem of the nature and the position of the anhydride rings in anhydrocellulose requires special study.

EXPERIMENTAL

Several samples of fibrous tosyl cellulose (p-toluenesulfonic esters of cellulose) of different degrees of substitution were prepared, experiments performed on the action of sodium in liquid ammonia on them and the composition of the anhydro derivatives of cellulose formed and their acetates determined.

Preparation of tosylcellulose samples. For the syntheses we used normal purified (factory) cotton cellulose (viscosity 56 cp), which was first activated by precipitation from 3% cuprammonium solution or by mercerization in 18% sodium hydroxide, then washed with water and dried with dry pyridine, or heated in pyridine at 70° for 70 hours. The tosyl esters, used for the preparation of anhydrocellulose, were synthesized from cotton cellulose by the action of p-toluenesulfonyl chloride (m.p. 69°) in a pyridine medium. This gave fibrous esters, which

TABLE 1

Sample No.	Number of moles		Time (in hours)	Sulfur found (%)	Composition
	p-toluene-sulfonyl chloride per glucose unit	pyridine per glucose unit			
1	10	120	2	3.76	$C_6H_7O_2(OTs)_{0.25}(OH)_{2.75}$
2	5	20	5	8.06	$C_6H_7O_2(OTs)_{0.67}(OH)_{2.33}$
3	6 + 6	26	21	11.10	$C_6H_7O_2(OTs)_{1.18}(OH)_{1.82}$
4	6 + 6	26	21	12.70	$C_6H_7O_2(OTs)_{1.65}(OH)_{1.35}$

TABLE 2

Sample No.	Composition of anhydrocellulose	Found (in %)		Calculated (in %)		Composition of acetates	Acetic acid (in %)	
		C	H	C	H		found	calculated
1	$C_6H_7O_2(OH)_{2.5}a-O_{0.25}$	45.5	6.25	48.7	6.06	$C_6H_7O_{2.25}(OCOCH_3)_{2.45}$	56.6	56.7
2	$C_6H_7O_2(OH)_{1.66}a-O_{0.67}$	48.14	6.26	48.3	5.80	$C_6H_7O_{2.67}(OCOCH_3)_{1.62}$	44.8	44.7
3	$C_6H_7O_2(OH)_{1.2}a-O_{0.6}$	49.91	6.09	49.4	5.64	$C_6H_7O_{2.9}(OCOCH_3)_{1.15}$	35.5	35.6
4	$C_6H_7O_2(OH)_{0.9}a-O_{0.9}$	51.2	6.53	51.17	5.61	$C_6H_7O_{3.2}(OCOCH_3)_{0.57}$	20.8	20.8

facilitated the cleavage of p-toluenesulfonic acid groups. In our experiments at 15-20°, the regenerated cellulose (from cuprammonium solutions) gave, over 48 hours, cellulose esters with a sulfur content of 13-14% (degree of substitution 1.8-2.2), which were readily soluble in organic solvents. Cotton cellulose, mercerized in 18% sodium hydroxide for 2 hours, formed tosyl esters over 24-48 hours (with 7 moles of p-toluenesulfonyl chloride per glucose residue) with a degree of substitution of 1-2, but with a yellowish color.

Cellulose activated with pyridine by prolonged heating gave a degree of substitution of from 1 to 1.9 on repeated treatment with p-toluenesulfonyl chloride for from 2 to 21 days at 15-20°. At the end of the reaction, the tosylation mixture was poured into water or aqueous alcohol and the filtered product washed with water, methyl alcohol and ether. The samples obtained were insoluble in organic solvents and swelled in pyridine.

Table 1 gives the preparation conditions and composition of tosyl esters of cellulose (activation of cotton with pyridine), used for the synthesis of cellulose anhydrides.

The sulfur content of the cellulose tosyl esters was determined by oxidation with nitric acid and bromine, with a subsequent alkaline fusion and gravimetric analysis.

Cleavage of p-toluenesulfonic acid from tosylcellulose. A sample of tosylcellulose was placed in a reaction vessel, into which was condensed ammonia. Metallic sodium (6 g-atoms per glucose unit of the cellulose ester) in small pieces, which had been washed in dry ether, was introduced. The reaction lasted for 12-48 hours depending on the degree of esterification of the cellulose. The p-toluenesulfonic acid was cleaved completely from samples 1 and 2 of tosylcellulose in 12 hours; in the case of sample 3, 2 treatments of 12 hours each were required and the p-toluenesulfonic acid was completely cleaved from sample 4 after one treatment for 48 hours with 7.5 g-atoms of sodium per glucose unit of the molecule. From 25 to 75 ml of liquid ammonia was used per gram of tosyl ester.

The anhydro derivatives of cellulose obtained dissolved partially in Schweitzer's cuprammonium solution and in 10% sodium hydroxide, did not contain halogen or sulfur, did not rapidly decolorize a solution of potassium permanganate and contained less than 1% of methylpentosans.

The samples of anhydrocellulose obtained were acetylated with a mixture of acetic anhydride and acetic acid (14 g per g of anhydrocellulose) with a catalyst, perchloric acid, for 24 hours at 20°. The product did not

dissolve in the acetylating mixture, which is characteristic of the acetylation of cellulose with this acetylating mixture. The reaction mixture was poured into a 20-fold excess of cooled water to precipitate a colorless or slightly yellowish, fibrous product, which was washed with water, alcohol and ether. Samples were ground and sieved for analysis for acetyl groups. Analyses of the anhydrocelluloses and their acetates indicated that anhydrocelluloses of the given compositions had been obtained in our experiments.

Table 2 gives the compositions of the anhydrocelluloses and their acetates, which may be represented by the general formulas: $[C_6H_7O_2 + x(OR)_{3-2x}]_n$ or $[C_6H_7O_2(OR)_{3-2x}a-O_x]_n$, where a-O is the oxygen atom of the anhydro ring, x the number of them per glucose unit, and $3-2x$ the number of residual hydroxyls, while $R = H$ or $COCH_3$.

Despite some comparatively small discrepancies (in Table 2), especially for samples 3 and 4, one can consider that the compositions of the anhydrocelluloses and their acetates agree quite well, within the limits of normal analysis error.

SUMMARY

1. The action of sodium in liquid ammonia on p-toluenesulfonic (tosyl) esters of cellulose gave samples of anhydrocellulose. The composition of the anhydrocelluloses was confirmed by the analyses of the samples themselves and of their acetates, which satisfied the general formulas of the compounds obtained, within the limits of analytical error.

2. When tosyl esters of cellulose, containing more than 1 tosyl group per glucose unit, were treated with sodium in liquid ammonia, p-toluenesulfonic acid was cleaved with the formation of anhydro rings and other tosyl groups were hydrolyzed.

LITERATURE CITED

- [1] S. Peat, Adv. in Carb. ch. 2, 37 (1946).
- [2] F. Gardner and C. Purves, J. Am. Chem. Soc. 65, 444 (1943).
- [3] S. N. Danilov, XXVIII Congreso Intern. de Química industrial, II, 992 (1955).
- [4] A. A. Lopatenok, Syntheses of Desoxycelluloses, Anhydrocelluloses and Celluloseens and a Study of Their Properties, Diss. Lensoviet Tech. Inst. Leningrad (1953) [In Russian].
- [5] I. Mahoney and C. Purves, J. Am. Chem. Soc. 64, 9 (1942).

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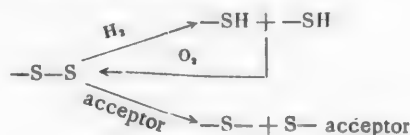
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THE CHEMISTRY OF XANTHATES AND VISCOSE

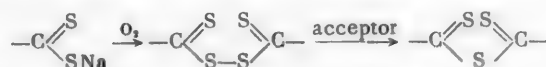
IX. THE DETECTION OF POLYSULFIDE COMPOUNDS IN VISCOSE AND THEIR ROLE

S. N. Danilov, N. F. Gintse and M. G. Okun'

Viscose, alkali cellulose and cuprammonium solutions of cellulose are outstanding among the different products and technical mixtures in complexity and the great peculiarity of the processes in them and the study of the latter is not only of technical, but also of serious theoretical scientific interest. They may be considered to some extent as models of biologically important systems in which an important role is played by oxidation and oxidation-reduction processes and also the phenomena of sulfur transfer and conversions between disulfides and mercaptan groups (conversions of cysteine and cystine and glutathione) [1].



As a result of oxidation by atmospheric oxygen, cellulose xanthate may form dioxanthates [2], which are then converted into cellulose thioanhydrides, which were first prepared in our laboratory [3, 4].



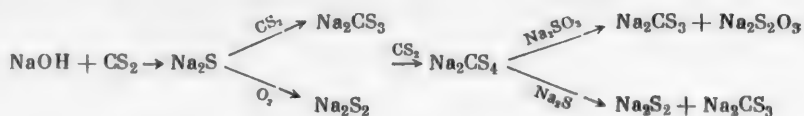
In our papers, data were presented indicating the role of sulfite as an antioxidant [5] and, in particular, as a sulfur acceptor in viscose [6]. Polysulfide compounds (sodium disulfide, perthiocarbonate and thiosulfate) were detected in viscose [7] by means of sodium sulfite and sodium sulfide — sulfur acceptors contained in viscose — by the use of sulfur acceptors foreign to viscose — sodium cyanide and sodium arsenite — and, especially, by the use of tracers [8]. These new facts make it possible to examine the phenomena occurring in viscose during its ripening in more detail.

During the xanthation of alkali cellulose, various sulfur-containing compounds are formed, which are converted by the action of atmospheric oxygen into polysulfide compounds (sodium disulfide, perthiocarbonate and thiosulfate and cellulose dioxanthate), capable of donating sulfur to acceptors [7]. Thus, by taking up oxygen, sodium sulfide is an accelerator of the oxidation of viscose components, while sodium sulfite and thiosulfate, like polythionates [6], act as antioxidants. Sodium sulfide, sulfite and possibly thiocarbonate participate in the cleavage of sulfur from polysulfide compounds (from dioxanthate and sodium disulfide, perthiocarbonate and thiosulfate).

As viscose ripens, substances accumulate in it in which the ratio of sulfur to sodium increases: from 1:2 (Na_2S , Na_2SO_3) to 1:1 (Na_2S_2 , $\text{Na}_2\text{S}_2\text{O}_3$), then to 3:2 (Na_2CS_3) and finally to 2:1 (Na_2CS_4), and also the amount of oxygen per sodium atom increases to 1.5–2 atoms ($\text{Na}_2\text{S}_2\text{O}_3$, Na_2SO_3 , Na_2SO_4). Sodium sulfite and thiosulfate and finally sodium sulfate are obtained as a result of viscose oxidation.

Apparently, it is precisely the oxidative processes which cause the accumulation of polysulfide compounds in viscose, though they may be partly formed due to free sulfur, if it is present in the technical carbon disulfide. Sodium trithiocarbonate is mainly formed by the reaction of sodium sulfide with carbon disulfide, though, in the

presence of oxygen, it may be formed from perthiocarbonate donating its sulfur atom to an acceptor. This is quite possible as sodium disulfide, formed from sodium sulfide by oxidative processes, reacts with carbon disulfide with a greater thermal effect than sodium sulfide [9].



The transfer of sulfur must also be considered in connection with oxidation phenomena in viscose. Other substances of reducing character can also affect viscose similarly to sodium sulfite [10], which is an antioxidant and sulfur acceptor in viscose, but only those, which are capable of adding sulfur, such as cyanides and arsenites [7].

Polysulfide compounds react with sodium hydroxide, which is, to some extent, a sulfur acceptor. Dixanthates and particularly thioanhydrides of cellulose are readily cleaved by alkali [8], and this is accompanied by oxidative cleavage of the dithio group. We previously showed that cleavage of dixanthates with alkali must accelerate the ripening of viscose due to the fact that only half of the cellulose xanthate is regenerated, while the second part of the dithiocarbonate grouping is cleaved [11]. Thus, in the reaction of both sodium disulfide and perthiocarbonate with alkali, one atom of oxygen must be liberated and this will oxidize primarily sulfur products.

It is quite probable that during xanthation and ripening of viscose, some part is played by the oxidizing and reducing groupings in the glucose chains of the cellulose molecules, formed during the preaging of the alkali cellulose, and also products of saccharinic rearrangement and the Cannizzaro reaction (under the action of alkali) of aldehyde groups, produced in alkali cellulose by oxidation. Similar simultaneous oxidation-reduction phenomena were described for the acid conversions of hydroxyaldehydes [12], such as the conversion of hydroxyisobutyraldehyde into isobutyric acid or into the corresponding glycol and hydroxyisobutyric acid. However, these problems have not yet been examined sufficiently for viscose.

Although there is no direct experimental proof as yet, there are grounds for thinking that the ripening of viscose is, in the first instance, the result of hydrolytic and thermal cleavage of dithio groups of xanthate and proceeds by radical- and chain-type reactions. This mechanism is particularly probable for oxidation-reduction processes and sulfur-transfer reactions. We may thus explain the rapidity of the ripening of viscose. The chain of these reactions must begin with oxidative conversion of cellulose xanthate and sodium sulfide (initial products). It continues with sulfur transfer to acceptors and cleavage of polysulfide compounds with the liberation of oxygen. Although polysulfide compounds are inevitably formed in viscose, they are rapidly decomposed in it also. Therefore, analysis indicates a small amount of polysulfide compounds in viscose [8].

Chemical conversions, which are of importance in the ripening of viscose, occur with cellulose xanthate, sodium sulfide, trithiocarbonate, etc.; for example:

- 1) the number of dithiocarbonate groups in the xanthate gradually decreases due to their hydrolytic cleavage and the liberation of carbon disulfide by the action of heat; the latter is again distributed between xanthate, sodium sulfide and alkali; the trithiocarbonate is partially hydrolyzed to form sodium carbonate and sulfide;
- 2) as a result of oxidative conversions and the transfer of sulfur atoms to acceptors (sodium sulfite and sulfide and alkali and partially trithiocarbonate), polysulfide and oxygen-containing substances accumulate;
- 3) cellulose dixanthate and thioanhydride are formed and polysulfide electrolytes transfer their sulfur to acceptors, which affects the distribution of carbon disulfide in the viscose;
- 4) polysulfide compounds are cleaved by reaction with alkali; this liberates oxygen, which again contributes to the formation of polysulfide compounds, that are also produced by external atmospheric oxygen; it is possible that the reducing groups of cellulose also participate in the conversions;
- 5) the ripening of viscose, as regards cleavage of dithiocarbonate groups and, in particular, oxidative phenomena and the transference of sulfur, proceeds as a radical and a chain process;
- 6) as a result of chemical conversions (impoverishment of the xanthate in dithiocarbonate groups and accumulation of electrolytes — soda and sulfur-containing salts) the solubility of the xanthate decreases and the viscosity, structuralization and ripeness of the viscose increase.

We should note that previous ideas on stabilizers and destabilizers of viscose require more accurate definition and we considered this in connection with the problem of the interaction of components in viscose. It is necessary to consider precisely the alkalinity of the medium, the whole complex of viscose components and the nature of the cation and anion of the salts [13]. The rate of decomposition of xanthate in the presence of electrolytes is connected with its precipitation in viscose. This phenomenon was previously considered as coagulation or gelling of the viscose.

As is known, the addition of sodium sulfite to viscose slightly retards the decomposition of xanthate in it and slightly less trithiocarbonate is formed, although the main direction of the reactions during ripening is largely maintained. The ripeness according to the salt index and the ammonium chloride number and also the viscosity of the viscose are slightly reduced by the addition of sulfite. The colloidal-chemical action of sulfite is connected with its salt-electrolyte nature and its chemical action as a sulfur acceptor and an antioxidant, which hinders the formation and accumulation of polysulfide compounds in viscose. As previous experiments in our laboratory showed, due to this the addition of sulfite to viscose makes it possible to raise the concentration of cellulose in viscose (to 9-9.5%) and slightly lowers the evolution of carbon disulfide during spinning.

In his time, E. Heuser put forward the theory that the reduction in the viscosity of viscose after oxygen has been passed through it, if it is not connected with destruction of the cellulose, may be explained by changes in the "coagulating" action of the mineral components of viscose, due to their oxidation [14]. In the light of the information presented above, in the absence of cellulose destruction, the reduction in the viscosity of viscose may indicate that the oxidation of viscose components proceeds mainly in the direction of sulfite formation.

We should note that the addition of other sulfur acceptors (sodium arsenite and especially cyanide) to viscose also retards the ripening of viscose, raises the salt index and lowers the viscosity of viscose. However, if sodium sulfite, cyanide and arsenite are added to 2% aqueous solutions of purified xanthate in amounts of 0.3 to 0.5% of the solution weight, then the gelling of solutions is accelerated (experiments of A. F. Vorob'eva). This is additional confirmation of the fact that the action of sulfite on viscose is mainly connected with chemical action with viscose components and not with its role as an electrolyte.

We previously reported the role of the alkalinity of the solution in the action of electrolytes (viscose components) on the ripening of viscose and solutions of purified xanthate [13].

The introduction of polysulfide substances into viscose affects its viscosity and the salt number of its ripeness, but in the opposite way to the introduction of sulfur acceptors. According to experiments (of E. Shimanskaia) in our laboratory, which for brevity we will not describe, the introduction of polysulfide compounds [sodium (perthiocarbonate and disulfide)] into viscose in amounts of 0.3-0.5% of the weight of viscose produces a rapid gelling of the viscose with the effect falling in the series:



To detect and determine the amounts of polysulfide compounds in viscose, we tried potentiometric and spectrographic methods and also chromatography. It was found that the donors and acceptors of sulfur in viscose are interconnected and form three pairs of substances, which are determined together by potentiometric titration: 1) Na_2SO_3 and $\text{Na}_2\text{S}_2\text{O}_3$, 2) Na_2S and Na_2S_2 , 3) Na_2CS_3 and Na_2CS_4 . This hinders their separate quantitative determination. The determination of polysulfide compounds is particularly unreliable in the presence of alkali and soda, probably due to chemical interaction.

The spectra of viscose components, including polysulfide compounds, are quite characteristic, making it possible to determine disulfide and perthiocarbonate in viscose.

1. Determination of Polysulfide Compounds in Viscose

(From the experiments of N. F. Gintse and with the participation of V. V. Vinogradova)

In addition to the usual methods of viscose analysis, based on iodometry in conjunction with methods of precipitating viscose components in the form of cadmium and zinc salts and on determinations of carbon disulfide and hydrogen sulfide with decomposition of the viscose by mineral acid, a method of characterizing viscose by potentiometric titration has been developed recently. In recent years attempts have been made to analyze viscose chromatographically and especially to separate xanthate from low molecular components by means of ion-exchange

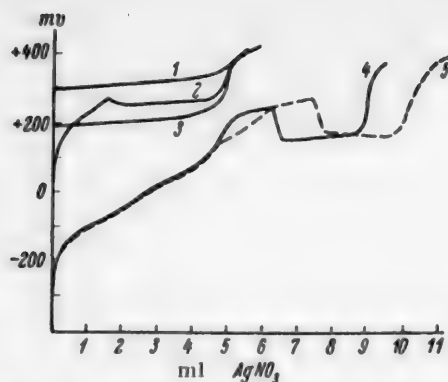


Fig. 1. Potentiometric titration of aqueous solutions of salts and sodium hydroxide with silver nitrate.

1) Sodium carbonate; 2) sodium sulfite; 3) sodium hydroxide; 4) sodium thiosulfate; 5) a mixture of sodium sulfite and thiosulfate.

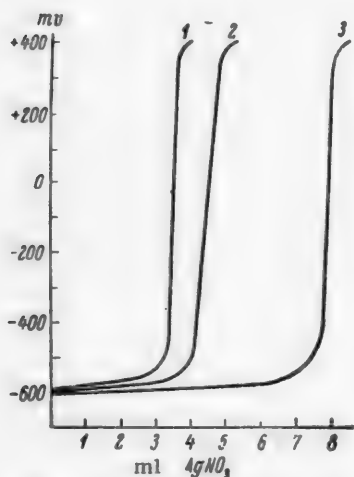


Fig. 2. Potentiometric titration with silver nitrate of aqueous solutions of sodium trithiocarbonate and perthiocarbonate.

1) Trithiocarbonate; 2) perthiocarbonate; 3) mixture of trithiocarbonate and perthiocarbonate.

resins [15]. Methods have been developed in our laboratory for the total determination of polysulfide compounds, based on their donation of a sulfur atom to acceptors, such as sodium cyanide, sulfite and arsenite [6-8]. In looking for methods of determining polysulfide compounds separately, we examined the potentiometric titration of viscose and model solutions of its components by silver nitrate with a silver electrode and also attempted to find conditions for the chromatographic separation of viscose components. The results of these experiments are presented below.

Figure 1 shows titration curves of aqueous solutions of the first pair of viscose components which interested us, namely sodium sulfite and thiosulfate, and also of sodium hydroxide and carbonate, which are titrated in a nearby potential region. We should note that in the titration of aqueous solutions of sulfite we had to add an oxidation inhibitor (0.005 mole/liter of ethylenediamine-tetraacetic acid) to suppress oxidation of the sulfite during the titration so as to obtain reproducible results. In the presence of inhibitor, readily reproducible results were obtained, which agreed accurately with the data of iodometric analysis. The presence of an ascending section on the sulfite titration curve in the range from 0 to +250-280 mv is caused by solution of the silver sulfite formed in excess sodium sulfite to form a binary salt. It is recommended that the determination of thiosulfate by potentiometric titration with silver nitrate using a silver electrode is performed in the presence of sodium acetate at 0° or 80-90° [16] and it is stated that the equilibrium potentials are established slowly due to decomposition of the initially formed binary sodium silver thiosulfate with the formation of silver sulfide. The jump in potential at the end of the titration occurs at a ratio of $\text{Ag}^+ : \text{S}_2\text{O}_3^{2-} = 1:1$. At normal temperature and in the absence of additions, the titration curve of thiosulfate (Fig. 1) has a completely ascending section in the potential range from -200 to +250 mv (formation of binary salt), a small plateau at +250 mv, a peak with a reverse potential jump and a longer plateau at +160 - 180 mv (decomposition of binary salt). The titration ends with a $\text{Ag}^+ : \text{S}_2\text{O}_3^{2-}$ ratio of about 2:1. The first portion of the curve ($\text{Ag}^+ : \text{S}_2\text{O}_3^{2-}$ ratio = 1:1) is always reproduced well in parallel determinations and the second, with less accuracy. Equilibration of the potentials occurs very slowly throughout the whole titration. The variation in potential in the region of the ascending section of the curve, ending in the peak with the reverse potential jump, is so characteristic that it makes it possible to detect

thiosulfate in very small amounts, for example, as very slight traces in preparations of sodium sulfide and disulfide or thiocarbonates. However, the positions of the titration curves of thiosulfate and sulfite and the configurations of these curves are so similar that it is impossible to distinguish sulfite in mixtures with thiosulfate. The combined curve of a mixture of these components differs little from the titration curve of thiosulfate solution (Fig. 1). In the determination of these components in viscose, the problem is further complicated by the proximity of the titration region of sodium hydroxide (+220-240 mv) and soda (+300 mv). The old method of determining thiosulfate and sulfite by Kurtenaker's procedure cannot be replaced by the potentiometric method.

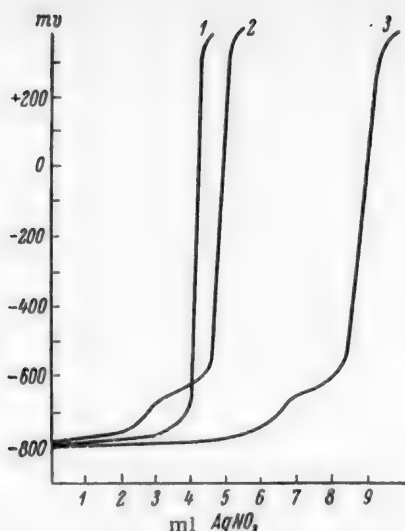


Fig. 3. Potentiometric titration with silver nitrate of aqueous solutions of sodium sulfide and disulfide. 1) Sulfide; 2) disulfide; 3) mixture of sulfide and disulfide.

Figures 2 and 3 show the silver nitrate titration curves of aqueous solutions of sodium sulfide and disulfide and tri- and perthiocarbonates. Each of these components is titrated accurately and clearly alone and gives a sharp potential jump at the equivalence point with good agreement between the potentiometric and iodometric determinations. We previously reported [13] that the potentiometric determination of trithiocarbonate was possible only as the total with perthiocarbonate and sulfide, with disulfide. The titration curves of aqueous solutions of trithiocarbonate and perthiocarbonate are completely identical, as can be seen, and merge into one continuous curve in the titration of a mixture of these salts (Fig. 2). The total content of these salts of an aqueous solution was determined quite accurately.

The titration curve of sodium disulfide differs from that of sodium sulfide in the presence of an additional plateau at +650 mv (Fig. 3). The first plateau corresponds to the precipitation of silver sulfide ($\text{Na}_2\text{S} + 2\text{Ag} \rightarrow \text{Ag}_2\text{S} + \text{S}$) and the second (in the opinion of Sack [17]) is caused by the discharge of colloidal particles of $\text{Ag}_2\text{S-S}$. When alkali is added to the disulfide solution, this plateau disappears. In the titration of a mixture of aqueous solutions of disulfide and sulfide, there is a quantitative merging of the main plateaus of the individual curves, but the character of the additional disulfide plateau is

retained (Fig. 3). Thus, while it is impossible to separate sulfide and disulfide quantitatively in mixtures, it is possible to detect disulfide in them qualitatively. The disappearance of the second plateau on the titration curve of disulfide on the addition of alkali, makes it impossible to detect disulfide even qualitatively in alkaline solutions and consequently in viscose from potentiometric-titration curves. We should note that the presence of sulfide or disulfide in mixtures of tri- and perthiocarbonate does not interfere with the determination of the latter by potentiometric titration with silver nitrate and likewise, the presence of tri- or perthiocarbonates in the solution does not interfere with the determination of mono- and disulfide.

In the potentiometric titration of alkaline solutions of disulfide [13], trithiocarbonate and perthiocarbonate with silver nitrate, high results are obtained as a certain amount of alkali (up to 2 moles per mole of salt) is titrated together with the salt. This phenomenon was reported for solutions of trithiocarbonates by Herrent and Inoff [18] and Zav'ialova [19], but in a slightly different qualitative ratio by the latter. We titrated mixtures of trithiocarbonate, disulfide and perthiocarbonate with sodium hydroxide, prepared immediately before titration, over a wide range of potentials, which made it possible for us to observe the changes in the precipitation plateaus of sodium hydroxide. The latter were noticeably decreased in the presence of each of the given salts and with a sodium hydroxide content of less than 2 moles per mole of salt in the mixture, they disappeared completely. The precipitation plateaus of the salts increased correspondingly and reached a maximum at slightly less than double the original value, with a sodium hydroxide content in the mixture of 2 moles per mole of salt. With a further increase in the alkali content, the values of the plateaus of disulfide hardly changed and the plateaus of the thiocarbonates contracted slightly. These phenomena are connected with the partial decomposition of the salts during the titration as is indicated by the course of titration curves of mixtures. A new region of difficultly establishable potentials in the range from -300 to +200 mv appears on all the curves and, in the presence of trithiocarbonate or perthiocarbonate, a new plateau appears in the region of sodium carbonate precipitation. With an increase in the alkali content of the mixture, the decomposition of the salts increases. The results of our experiments on the titration of alkaline solutions of disulfide, perthiocarbonate and trithiocarbonate, which show that 2 moles of sodium hydroxide are titrated with 1 mole of each of the salts, agree with the data of Herrent and Inoff [18] on trithiocarbonate.

The instability of disulfide and perthiocarbonate, observed in alkaline solution, results in a low content of

polysulfide compounds in the viscose (the fact that cellulose dioxanthate is readily decomposed in alkali was reported previously [2, 11]). As we saw, the decomposition of polysulfide salts results in the bonding of free sodium hydroxide.

Experiments showed that direct potentiometric titration of viscose with silver nitrate was only of limited application for characterizing the composition of viscose and, in particular, it could not be used for the determination of its polysulfide components.

The problems in the use of chromatographic methods for the separate determination of viscose components were not considered in the works of Samuelson and Geiger [15], that were mentioned. The specific properties of viscose components, their diversity, and most of all, low stability, exclude the use in analysis of lengthy operations and high dilutions and raise considerable difficulties in the choice of reagents for chromatographic analysis of viscose. Since the components of viscose are salts of strong bases and weak acids, then for ion exchange with them under alkaline conditions, it is only possible to use ion-exchange resins with strongly basic ionogenic groups, for example, with quaternary ammonium-base groups, which are clearly monofunctional. Samuelson and Geiger used Amberlite IRA-400 and Dowex-1.

The strongest anionite of our resins is PEK, but it only has low mechanical strength in the wet state and therefore we also used two slightly less strong anionites, PE-9 and EDE-10, in our experiments. The experiments were performed with the hydroxyl form of the resin in ion-exchange columns of the normal type with a fitting ensuring filtration at constant pressure. The experiments showed that all three resins readily exchanged with trithiocarbonate and perthiocarbonate and more difficultly with sulfides, especially the resin EDE-10. For each of the resins investigated, working conditions were found so that the side products were removed quantitatively from the viscose and completely pure xanthate was obtained as filtrates containing only sodium hydroxide in addition to the xanthate. The least advantageous were the conditions for the resin EDE-10, due to its low capacity for exchange with sulfide. The use of the resins PEK and PE-9 gave similar results. The separation of the viscose components absorbed on the anionite layer presented considerable difficulty, largely due to the necessity for diluting the viscose considerably for filtering it through the anionite. Special experiments proved that there was no change in the total distribution of sulfur between the xanthate and the side products during operation on the ion-exchange columns. In this respect, the use of activated charcoal was more favorable as it made it possible to work with less dilute viscoses and at higher filtration rates. Filtration of viscose through activated charcoal quantitatively removed all the side products except thiosulfate; in contrast to ion-exchange resins, charcoal held sulfides more readily than thiocarbonates. Attempts to separate the absorbed components by elution in stages using different salt solutions and certain solvents, did not give positive results, however, in this case.

Further investigations are required on the sorption and chromatographic methods of elucidating the composition of viscose.

2. Spectroscopic Investigations of Viscose

(From the experiments of M. G. Okun')

The investigations of viscose and trithiocarbonate, carried out by Rassow and Aehnelt in the ultraviolet region, are well known [20].

Our spectrographic investigations over a wide range of wavelengths were aimed at examining the spectra of polysulfide compounds (sodium disulfide and perthiocarbonate), as a method of detecting them in viscose. An investigation was made of the absorption spectra of aqueous and alcoholic solutions of sodium disulfide, perthiocarbonate and trithiocarbonate and mixtures of these sulfur-containing substances and also water-diluted industrial viscose and similar solutions to which polysulfide compounds had been added preliminarily.

The experiments were performed on an SF-11 spectrophotometer and the optical density was determined in the visible and ultraviolet parts of the spectrum, using hermetically sealed cells with quartz windows. In all the experiments, the layer thickness equalled 5 mm. An incandescent tungsten filament lamp was used as a light source for the visible region and a hydrogen lamp for the ultraviolet region. The short-wave part of the spectrum was registered on an antimony-cesium photocell and the long-wave part on an oxygen-cesium photocell. The absorption spectrum of a substance was determined by measuring the relative value of the light beam, passing through the absorbing substance, relative to the wavelength.

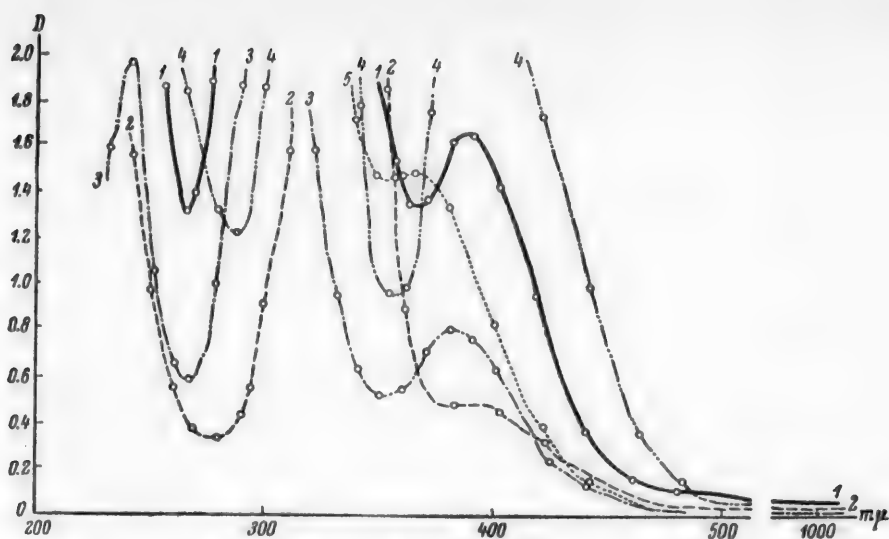


Fig. 4. Dependence of optical density of solutions on wavelength. 1) Aqueous solution of viscose; 2) aqueous solution of sodium trithiocarbonate; 3) alcohol solution of sodium trithiocarbonate; 4) aqueous solution of sodium perthiocarbonate; 5) aqueous solution of sodium disulfide.

An investigation was made of viscose solutions diluted 50, 100 and 200 times and also of trithiocarbonate, disulfide and perthiocarbonate in the form of 0.05, 0.005 and 0.001 molar solutions. The clearest picture was given by viscose solutions diluted 200 times and for separate components, 0.001 molar solutions were convenient.

For the work, sodium perthiocarbonate, trithiocarbonate and disulfide were synthesized in an atmosphere of nitrogen recording to published descriptions [9]. The optical density was determined. Curves were constructed for the dependence of the optical density (D) on the wavelength (λ) (in $m\mu$). Measurements were performed at intervals of 5-10 $m\mu$. Blank readings were performed on the absorption of air in the measurement of the optical density of a solution or on a viscose solution of the same dilution for measurement of the absorption curves of substances dissolved in viscose.

Figure 4 shows the absorption curves for 0.001 molar solutions of polysulfide compounds, transmitting light over a wide wavelength range. An aqueous solution of trithiocarbonate has an absorption minimum at 280 $m\mu$. In the range from 310-350 $m\mu$, the optical density is very great; at 370 $m\mu$ the optical density falls sharply; in the range from 370-400 $m\mu$, it is almost constant and then becomes very small (asymptotically approaching the abscissa). An aqueous solution of perthiocarbonate has two absorption minima, one at 290 $m\mu$ and the other at 360 $m\mu$; in the ranges 300-340 $m\mu$ and 380-410 $m\mu$, the optical density is very large; at 410 $m\mu$ the density decreases considerably and then the optical density curve of the solution approaches the abscissa asymptotically. In the range 350-370 $m\mu$, an aqueous solution of sodium disulfide has an almost constant optical density, which then decreases sharply and then remains constant. The diluted viscose solution has an absorption minimum at 270 $m\mu$, the optical density of the solution is very great in the range 280-350 $m\mu$, in the range 350-400 $m\mu$, at 370 $m\mu$ —there is a minimum and at 390 $m\mu$ a maximum in the optical density and then the optical density of the solution is small.

A comparison of the absorption curves of polysulfide compounds and viscose shows that there is a great similarity in the course of the curves. In the range 240-300 $m\mu$, the optical density of trithiocarbonate is very small, while that of perthiocarbonate solution is considerable. As Fig. 4 shows, the optical density of viscose solution is almost equal to that of perthiocarbonate solution. In the range 300-320 $m\mu$, the optical density of polysulfide compound solutions is very great and viscose solution does not transmit light in this region. In the range 320-370 $m\mu$, the optical density of trithiocarbonate solution is very small. The optical density of viscose is considerably greater in this region. This is explained by the presence of disulfide compounds in the solution. As Fig. 4 shows, in this region the optical density of sodium disulfide solution determines the optical density of viscose solution.

In the range 370-420 m μ , the course of the optical density curve of viscose solution is analogous to that of trithiocarbonate solution. The great optical density of perthiocarbonate solution does not determine the optical density of viscose solution in the range 370-420 m μ , which is explained by the low concentration of perthiocarbonate in viscose. Comparison of the data obtained indicates that sodium disulfide, trithiocarbonate and perthiocarbonate are present in viscose solution.

Absorption curves of trithiocarbonate in absolute alcohol were plotted to exclude the hydrolysis of trithiocarbonate. The optical density curve of this solution has a sharply expressed minimum and maximum and differs considerably from the curve of the aqueous solution in the range 340-420 m μ . In the range 340-420 m μ , the appearance of the optical density curve of an aqueous solution of trithiocarbonate is similar to that of a sodium disulfide curve, i.e., an aqueous solution of trithiocarbonate contains disulfide due to hydrolysis and oxidation. Spectroscopic investigations of viscose and solutions of polysulfide compounds indicate the presence of polysulfide compounds in viscose.

As was previously stated, sodium disulfide appears in diluted aqueous solutions of trithiocarbonate and this must be considered in connection with the use of viscose dilution in the determination of polysulfide compounds in it. Experiments with viscose (N. F. Gintse) showed that the content of polysulfide compounds increased more considerably (1.5-2 times with a dilution of 12-fold) during the ripening of dilute viscoses than for normal viscoses.

SUMMARY

1. There are oxidation-reduction conversions and sulfur-transfer phenomena in viscose, especially in the presence of atmospheric oxygen, which give grounds for considering the ripening of viscose as a model for biologically important systems.
2. While the total content of polysulfide compounds in viscose can be determined with sodium cyanide and sulfite, their separate determination by the potentiometric method presents great difficulties, especially in the presence of alkali. Xanthate may be freed from side products by the use of active charcoal and anionites.
3. The courses of the optical density curves of viscose and trithiocarbonate solutions are analogous; in aqueous solutions of trithiocarbonate, sodium disulfide appears, due to hydrolysis and oxidation.
4. Trithiocarbonate is present in viscose solution in large amounts and perthiocarbonate in small amounts.

LITERATURE CITED

- [1] F. Hopkins, *Biochem. J.* 19, 787 (1925).
- [2] S. N. Danilov and N. M. Grad, *J. Gen. Chem.* 17, 2193 (1947).
- [3] S. N. Danilov and D. S. Brokhina, *J. Gen. Chem.* 4, 995 (1934).
- [4] S. N. Danilov, N. M. Grad and V. O. Klesman, *J. Appl. Chem.* 22, 625 (1949).
- [5] S. N. Danilov, N. M. Grad and E. I. Geine, *J. Gen. Chem.* 19, 826 (1949).*
- [6] S. N. Danilov and S. M. Rizov, *Ind. Org. Chem. No. 12*, 693 (1937).
- [7] S. N. Danilov, N. M. Grad and A. F. Vorob'eva, *J. Gen. Chem.* 19, 1257 (1949).*
- [8] S. N. Danilov, N. F. Gintse and K. V. Levitskaia, *J. Gen. Chem.* 28, 2948 (1958).*
- [9] E. W. Jeoman, *J. Chem. Soc.* 119, 38 (1921).
- [10] L. I. Mirilas, *Lotareichik, Artificial Fiber*, No. 4, 12 (1932).
- [11] S. N. Danilov and O. P. Koz'mina, *J. Appl. Chem.* 19, 1071 (1946).
- [12] S. N. Danilov and E. D. Venus-Danilova, *J. Gen. Chem.* 3, 559 (1933).
- [13] S. N. Danilov and N. F. Gintse, *J. Gen. Chem.* 27, 3290 (1957).*
- [14] E. Heuser, *The Chemistry of Cellulose*, London, 1944, p. 370.

*Original Russian pagination. See C. B. Translation.

- [15] O. Samuelson and F. Gärtner, *Acta chem. Scand.* 5, 596 (1951); E. Geiger and B. J. Weiss, *Helv. Chim. Acta.* 36, 2009 (1953).
- [16] Muller, Z. *anorg. Chem.* 134, 202 (1924).
- [17] W. Sack, *Fres. Ztschr. f. anal. Chem.* 131, No. 3, 199 (1950).
- [18] P. Herrent and G. Inoff, *J. Polymer Sci.* 3, 834 (1948).
- [19] N. N. Zav'ialova and A. B. Pakshver, *Exch. of Tech. Exp. Synth. Fiber*, 1, 32 (1952).
- [20] Rassow and Aehnelt, *Cellulosechemie*, 11, 169 (1929).

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THE FORMATION OF PEROXIDES IN THE OXIDATION OF CELLULOSE ETHERS AND ESTERS*

O. P. Koz'mina, V. I. Kurliankina, E. N. Matveeva and M. K. Aleksandrovich

As was reported in the paper of Danilov and Koz'mina [1] and in subsequent papers [2, 3 and 4], the destruction of cellulose ethers and esters at moderately elevated temperatures and by ultraviolet radiation is caused by their reaction with atmospheric oxygen, which leads to oxidation, cleavage of the oxidized ether or ester group and destruction of the chain. The oxidized ether and ester samples gave a positive reaction for peroxides and it can be postulated that the decomposition proceeds through the intermediate formation of peroxides.

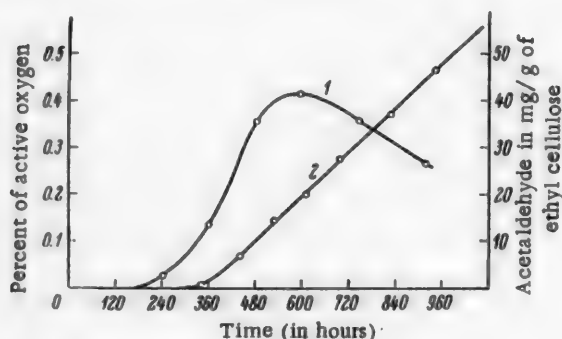


Fig. 1. Oxidation of ethyl cellulose at 70°. 1) Rate of peroxide formation; 2) rate of aldehyde formation.

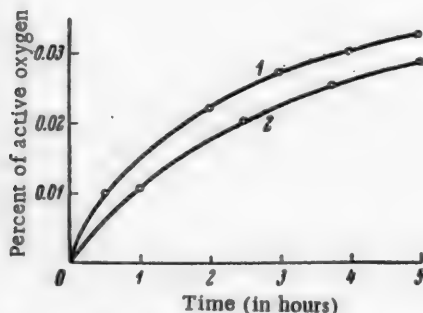


Fig. 2. Rate of peroxide formation in cellulose ethers and esters in ultraviolet light. 1) In acetobutyrate; 2) in ethyl cellulose.

In the course of further investigations, conditions for peroxide accumulation in cellulose ethers and esters were found and also the character of their formation rate curves, which had a definite maximum (Fig. 1, curve 1). In the same figure, curve 2 shows the rate of acetaldehyde formation in the same experiment. The curves indicate that peroxides were formed first. This is also indicated by direct experiment on the decomposition of peroxide groups in samples of oxidized ethers and esters in an atmosphere of nitrogen.

Peroxides of ethers and esters, especially of esters, are readily obtained by ultraviolet irradiation (Fig. 2). Our experiments show that peroxides of cellulose ethers and esters are comparatively and can be stored for a long period, both as the solid and in solution, which makes it possible to free them from traces of low-molecular substances by dialysis.

Peroxides of ethers and esters, and also their decomposition products — volatile peroxides and aldehydes — gradually accumulate during storage of the ethers and esters and reduce the induction periods of the thermo-oxidative decomposition of the ethers and esters. If the peroxide groups are destroyed with hydrogen iodide or hyposulfite and the low-molecular impurities washed out by dialysis [2] or the solutions of aged ethers or esters are treated with small amounts of salts of metals of variable valence (KMnO_4 , or acetates of iron and copper), which are subsequently removed, then induction periods again appear, as are characteristic of freshly prepared samples (Fig. 3).

*Report V in the series "Investigations in the field of oxidation processes of cellulose ethers and esters with molecular oxygen."

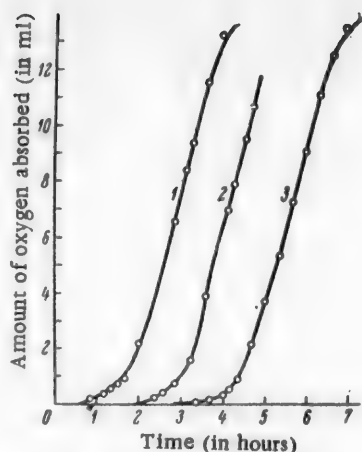


Fig. 3. Effect of preliminary treatment of solutions of aged samples of ethyl cellulose with solutions of variable-valence metal salts on the length of the induction period during oxidation at 130°.

- 1) Oxidation rate of original sample;
- 2) oxidation rate of sample treated with copper acetate; 3) oxidation rate of sample treated with iron acetate.

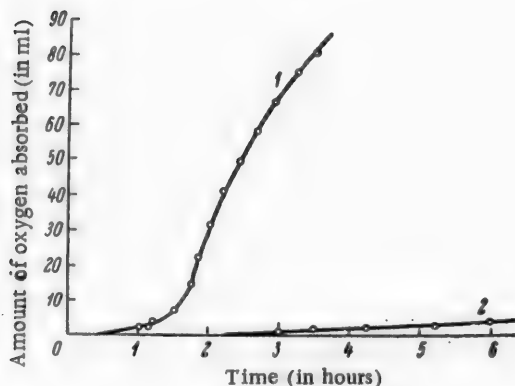


Fig. 4. Inhibiting effect of ferric salts in the oxidation of ethyl cellulose at 130°.

- 1) Oxidation rate of original sample; 2) oxidation rate of ethyl cellulose sample containing 1.8% of iron acetate.

placed on both sides along the faces of the cell at a distance of 20 cm. Figure 2 shows the rate of formation of peroxides of esters and ethers during irradiation at 25°. The peroxide groups were determined iodometrically after preliminary dialysis or evacuation of the samples in high vacuum to remove adsorbed low-molecular impurities.

The reaction with the peroxides, apparently, also explains the inhibiting effect of salts of variable-valence metals and sol impurities (iron) in technical samples of cellulose ethers and esters (Fig. 4).

On the basis of peroxidated ethers and esters of cellulose, the authors and V. I. Gribkova prepared graft polymers with styrene, methyl methacrylate and other monomers with from 2 to 10% of the grafted polymer chains, depending on the amount of peroxide groups in the original ether and ester samples. The formation of graft polymers is a further indication of the presence of peroxides in cellulose ethers and esters.

New data were obtained on the liberation (into the volatile phase [3]) of large amounts of peroxides (up to 30%) during oxidation of the esters and ethers under mild conditions, which probably also throws light on the character of the peroxides of the esters and ethers themselves.

The peroxides formed may serve as a source of formic acid, alcohols and hydrocarbons, as secondary products of the thermo-oxidative decomposition of ethers and esters.

EXPERIMENTAL

For the investigation we used industrial samples of ethyl cellulose with an ethoxyl content of 47.5-48.5%, which were first freed from sol impurities (up to 0.008-0.02%) by precipitation from acetic acid solution with dilute (10%) acetic acid. The cellulose esters were prepared from cotton cellulose of satisfactory purity and then purified in some cases only for comparison. The cellulose acetobutyrate contained 38-45% of butyric and 18-28% of acetic acids.

Preparation of peroxides of cellulose ethers and esters. For preparation of the peroxides, the ethers and esters in thin layers or films were heated or irradiated in a thermostated silica cell in a stream of oxygen, by the method described previously [3]. The most convenient temperature for the dark reaction was 70-90° and at this temperature the greatest amount of peroxides accumulated and it was possible to follow the different rates of their formation and decomposition (Fig. 1); the latter became the same with an increase in temperature. The source of ultraviolet light was PRK-4 lamps

Decomposition of peroxides of cellulose ethers and esters in nitrogen. The samples of ethers and esters, containing peroxide groups, were heated in a stream of nitrogen at 130°, when the peroxide groups decomposed, the characteristic viscosity fell (for example, from 2.0 to 1.8 for a sample of ethyl cellulose) and traces of aldehydes were detected colorimetrically.

Low-Molecular (volatile) peroxides from the oxidation of cellulose ethers and esters. Ethyl cellulose was oxidized in a stream of oxygen at 110° in the form of films and a thin layer of powder (in the oxidation of a thick layer, the peroxide yield fell sharply) and the low-molecular, volatile products were condensed at - 80°. To separate the peroxides, the condensate of the volatile products was dissolved in ether. The acids, alcohol and water were removed with CaCO₃, CaCl₂ and Na₂SO₄. The ether solution was distilled in high vacuum without heating, then the ether was evaporated and the peroxide concentrated in the residue.

The volatile peroxide had a specific, sharp smell, dissolved readily in ether, alcohol and water, reacted vigorously with lead tetraacetate and was rapidly extracted with alkali solution from organic solvents. At the same time, it reacted sluggishly with potassium iodide in acetic acid, though the iodine was liberated completely on long standing or heating. All these features are characteristic of hydroxyalkyl peroxides [5, 6].

The hydroxyalkyl character was confirmed by the immediate decomposition of the peroxide by mineral acids with the liberation of acetaldehyde [7]. In contrast to dihydroxyethyl peroxide, the peroxide obtained gave 1 mole of acetaldehyde on decomposition; thus, for example, when decomposed with hydrochloric acid, an aqueous solution containing 0.06615 mmole/ml of peroxide gave 0.06586 mmole/ml of acetaldehyde. Acetaldehyde was also liberated on treatment of the peroxide with SO₂. Volatile peroxides were also obtained in the oxidation of cellulose esters.

Effect of variable-valencesalts on the oxidation of ethyl cellulose. To acetic acid solutions of aged ethyl cellulose, with reduced induction periods, were added copper and iron acetates (ferric form) and also KMnO₄. The acetates were prepared by dissolving the hydroxides in glacial acetic acid and the solutions added to ethyl cellulose in acetic acid. The solutions were kept for a day (with KMnO₄, for a longer time — until it was reduced) and then the ethyl cellulose was precipitated with 10% acetic acid. Samples containing traces of iron (0.0115%) and not containing copper and manganese, had longer induction periods in comparison with the originals (Fig. 3), when oxidized as powders and films, prepared on glass. Addition of the oxidized forms of variable valence salts (also as acetates) in amounts of from 0.5 to 2% slows the thermo-oxidative process of ethyl cellulose. Figure 4 shows curves of the oxygen absorption of the original sample and one with 1.18% of iron acetate added.

LITERATURE CITED

- [1] S. N. Danilov and O. P. Koz'mina, *J. Gen. Chem.* 18, 1823 (1948).
- [2] O. P. Koz'mina, V. I. Kurliankina and E. N. Matveeva, *Proc. Acad. Sci. USSR* 144, 789 (1957). *
- [3] O. P. Koz'mina and V. I. Kurliankina, *J. Appl. Chem.* 31, 601 (1958).*
- [4] O. P. Koz'mina and V. I. Kurliankina, *J. Appl. Chem.* 31, Vol. 11 (1958).*
- [5] A. Riche, *Alkylperoxyde und Ozonide*. Dresden (1931).
- [6] K. I. Ivanov, *Intermediate Products and Intermediate Reactions in the Auto-Oxidation of Hydrocarbons* (1949) [In Russian].
- [7] H. Wieland and A. Wiegler, *Lieb. Ann.* 431, 301 (1923).

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*Original Russian pagination. See, C. B. Translation.

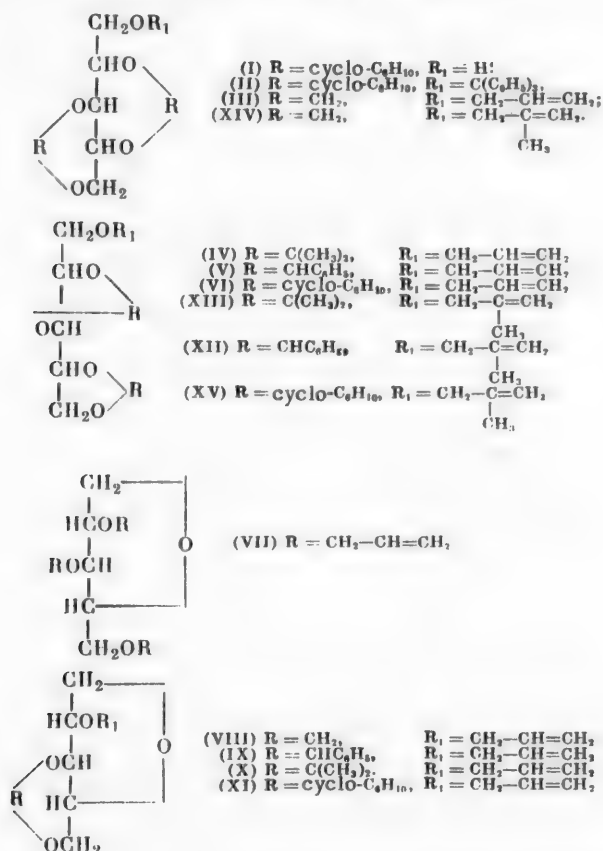
ALLYL AND METHALLYL ETHERS OF ACETALS AND KETALS OF XYLITOL AND XYLITAN*

A. N. Anikeeva and G. M. Zarubinskii

The allyl and methallyl ethers of a series of polyhydric alcohols and carbohydrates have been described, including those of α -methylglucoside [1] and galactoside [2], mannitol, sucrose [3] and others.

We synthesized the allyl and methallyl ethers of acetals and ketals of xylitol and xylitan by treating them with allyl bromide or methallyl chloride in a solvent in the presence of powdered sodium hydroxide. The starting materials—2,4-3,5-dimethylenexylitol [4], 2,3-4,5-diacetonexylitol [5] and 2,3-4,5-di-benzylidenexylitol [6] were prepared by the methods described in the literature.

All the xylitol derivatives given above have been shown to contain a free primary hydroxyl group; hence, there is no doubt that the position of the allyl and methallyl groups of the molecules of the derivatives obtained is at the first carbon atom. (Compounds III, IV, V, VI, XII, XIII, XIV and XV).



*This article is the 6th report in the series "Anhydrides, and amino- and guanido-derivatives of carbohydrates and polyhydric alcohols;" for the 5th report see J. Gen. Chem. 27, 2434 (1957).

TABLE 1

Allyl Ethers of Acetals and Ketals of Xylitol

Exp. No.	Compound	Boiling point (pressure in mm) or melting point	n_D^{20}	d_4^{20}	MRD		Yield (in %)		Analysis data (in %)		
					found	calculated			carbon	hydrogen	calculated
1	1-Allyl-2,4,3,5-dimethylenexylitol $C_{10}H_{16}O_5$ (III)	146°	—	—	—	—	54	—	55.52, 55.34	7.61, 7.71	7.46
2	1-Allyl-2,3,4,5-diacetoxexylitol $C_{14}H_{24}O_5$ (IV)	106 (0.5)	1.4496	1.0419	70.19	70.20	33	—	61.86, 61.61	9.10, 9.09	8.88
3	1-Allyl-2,3,4,5-dibenzylidenexylitol $C_{22}H_{24}O_5$ (V)	157	—	—	—	—	80	—	71.70, 71.86	7.21, 7.02	6.58
4	1-Allyl-2,3,4,5-dicyclohexylidenexylitol $C_{20}H_{32}O_5$ (VI)	152 (0.6)	1.4902	—	—	—	87	—	68.17, 68.20	8.73, 8.82	9.40
5	2,3,5-Triallylxylitol $C_{14}H_{22}O_4$ (VII)	105—106 (0.8)	1.4692	1.0090	69.93	69.70	75	—	66.00	8.80	8.68

TABLE 2

Allyl Ethers of Acetals and Ketals of Xylitol

Exp. No.	Compound	Boiling point (pressure in mm) or melting point	n_D^{20}	d_4^{20}	MRD		Yield (in %)	Analysis data (in %)		
					found	calculated		carbon	hydrogen	calculated
1	Allyl ether of methylenexylitol $C_9H_{14}O_4$ (VIII)	88° (I)	1.4750	1.1648	44.59	43.36	48	53.24, 52.90	7.44, 7.58	7.52
2	Allyl ether of benzylidenexylitol $C_{18}H_{18}O_4$ (IX)	157—158 (0.8)	1.5274	1.1495	69.98	70.03	40	68.93, 68.85	7.39, 7.19	6.87
3	Allyl ether of acetoxexylitol $C_{11}H_{18}O_4$ (X)	135 (I)	1.4652	1.0887	54.36	54.59	84	61.26, 61.46	8.67, 8.60	8.41
4	Allyl ether of cyclohexylidenexylitol $C_{14}H_{22}O_4$ (XI)	105—106 (0.8)	1.4886	1.1054	66.25	66.28	76	65.93, 66.10	8.97, 8.82	8.68

TABLE 3

Methallyl Ethers of Acetals and Ketals of Xylitol

Exp. No.	Compound	Boiling point (pressure in mm) or melting point	n_D^{20}	d_4^{20}	Yield (in %)	Analysis data (in %)			
						carbon		hydrogen	
						found	calculated	found	calculated
1	Methallyl ether of dibenzylidenexylitol (XII) $C_{23}H_{26}O_5$	148—149°	—	—	50	72.01, 72.19	72.26	6.98, 6.94	6.80
2	Methallyl ether of diacetonexylitol (XIII) $C_{15}H_{20}O_5$	154—157 (0.8)	1.4534	1.0322	20	62.35, 62.39	62.91	9.27, 9.03	9.15
3	Methallyl ether of dimethylene-xylitol (XIV) $C_{11}H_{16}O_5$	133—135	—	—	18	52.87, 57.68	57.41	7.74, 7.96	7.82
4	Methallyl ether of dicyclohexylidenexylitol (XV) $C_{21}H_{34}O_5$	144—147 (0.5)	1.4905	1.0996	56	68.90, 68.92	68.82	9.89, 9.74	9.35

Dicyclohexylidenexylitol, which we were the first to obtain, was synthesized under the conditions used in our experiments on the preparation of cyclohexylidenexylitol [7] (the reaction time was increased from 10 to 30 hours).

To solve the problem of whether there was a free primary hydroxyl group in dicyclohexylidenexylitol, its triphenylmethyl ether was prepared. This shows that the allyl and methallyl groups attached to dicyclohexylidene were at the first carbon atom (VI and XV).

In a previous report [7], we presented data showing that in acetals and ketals of xylitol, the primary hydroxyl group was involved in the formation of the ketal and, apparently, the acetal link, since it was not possible to prepare the trityl ether of any of the compounds. This was confirmed by experiments presented in the previous report, showing that the compounds remaining after hydrolyzing the ketal groups from ketal benzoates could not be oxidized with lead tetraacetate. Consequently, the allyl groups in acetals and ketals of xylitol must be at the second or the third carbon atom (VIII, IX, X, XI).

EXPERIMENTAL

To synthesize dicyclohexylidenexylitol, a mixture of 35 g of xylitol (m.p. 96°), 90 g of freshly distilled cyclohexanone, 200 ml of absolute ether and 5 ml of concentrated sulfuric acid were shaken for 30 hours. The acid was neutralized with soda, the solution evaporated and the residue vacuum-distilled twice. We obtained 38 g (53%) of dicyclohexylidenexylitol as a viscous sirup (I).

B.p. 193° (0.5 mm), n_D^{20} 1.4985.

Found % C 65.43, 65.48; H 9.46, 9.38. $C_{17}H_{22}O_6$. Calculated % C 65.40; H 9.90.

The triphenylmethyl ether of dicyclohexylidenexylitol was prepared by reacting 2.9 g of dicyclohexylidenexylitol, dissolved in 20 ml of dry pyridine, and 2.9 g of triphenylmethyl chloride for 48 hours. The reaction

mixture was poured into ice water and the viscous mass produced was dissolved in chloroform, washed with water and dried with baked sodium sulfate. The solution was evaporated in vacuum and the residue crystallized completely after 14 days. After two recrystallizations from ethyl alcohol, the triphenylmethyl ether (in the form of fine needles) had m.p. 108° (II).

Found %: C 77.50; 77.48; H 8.05, 7.87. $C_{36}H_{42}O_8$. Calculated %: C 77.94; H 7.57.

Synthesis of allyl and methallyl ethers. The allyl and methallyl ethers were synthesized under identical conditions. The starting material, solvent and powdered alkali were placed in a three-necked flask on an oil bath and fitted with a stirrer, a reflux condenser and a dropping funnel. The allyl bromide or methallyl chloride was added dropwise with vigorous stirring, while the bath was heated to 50-70°. When the halide had been added, the mixture was boiled for 8-10 hours. Then the flask was cooled, the reaction mixture diluted with water and the benzene layer washed, dried with sodium sulfate and evaporated. The residue was either vacuum distilled or recrystallized from alcohol. In most experiments, the allyl ethers were synthesized using the reaction components, ketal or acetal of xylitol, halide and alkali, in the ratio 1:3:4.

The ethers obtained were insoluble in water but soluble in the normal solvents. The properties of the allyl ethers of acetals and ketals of xylitol obtained are presented in Table 1.

For the synthesis of 1,4-anhydro-2,3,5-triallylxylitol, a mixture of xylitan (5 g) was stirred vigorously with allyl bromide (26 g), heated to 70°, then 40% aqueous alkali added from a dropping funnel over a period of 45 minutes and heating continued for 5 hours. The following day, the oily layer was separated from the water, washed free from alkali and dried with sodium sulfate. Two distillations in vacuum yielded 6.9 g (75%) of substance as a thick, colorless sirup.

The analysis corresponded to the formula of the triallyl ether of xylitan (VII).

B.p. 105-106° (0.8 mm), n_D^{20} 1.4692, d_4^{20} 1.0090, MR_D 69.93; calc. 69.70.
Found %: C 66.00, H 8.80. $C_{14}H_{22}O_4$. Calculated %: C 66.14; H 8.68.

Allyl ethers of acetals and ketals of xylitan. The starting materials — methylenexylitan, benzylidenexylitan, acetonexylitan and cyclohexylidenexylitan — were prepared as we described previously [7]. Their allyl ethers were prepared as described above. The characteristics of the allyl ethers of xylitan derivatives are given in Table 2.

Methallyl chloride was prepared by a method described in the literature [8], but with some simplification of the apparatus. The mixture of products obtained (isopropyl chloride, methallyl chloride and dichloroisobutane) was distilled twice on a column. The methallyl chloride obtained boiled at 72° and had the physical properties reported in the literature. The characteristics of xylitol derivatives are presented in Table 3.

The authors would like to thank Prof. S. N. Danilov for directing the work.

SUMMARY

We synthesized allyl and methallyl ethers of acetals and ketals of xylitol and xylitan, which are not described in the literature and are of interest as reactive, unsaturated derivatives of polyhydric alcohols and their anhydrides.

LITERATURE CITED

- [1] P. L. Nichols and E. Vanovsky, J. Am. Chem. Soc. 74, 1625 (1944).
- [2] Helferich and Gerder, Ber. 73, 532 (1940).
- [3] E. Vanovsky and P. L. Nichols, J. Am. Chem. Soc. 67, 46 (1945).
- [4] Hann and Ness, J. Am. Chem. Soc. 66, 670 (1944).
- [5] Tipson and Gretcher, J. Org. Chem. 8, 95 (1943).
- [6] Vittorio Brocca and Alfredo Dausi, Ann. Chem. (Rome) 44, 120 (1954).

[7] S. N. Danilov, A. N. Anikeeva, N. S. Tikhomirova-Sidorova and A. N. Shirshova, *J. Gen. Chem.* **27**, 2434 (1957).*

[8] Burgin, Engs and Groll, *Ind. Eng. Chem.* **31**, 1413 (1939).

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AMINO DERIVATIVES OF 1,4-ANHYDROXYLITOL*

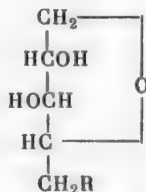
N. S. Tikhomirova-Sidorova and G. E. Ustiuzhanin

As a development of our previous communication [1], we prepared amino derivatives of xylitan from its chlorohydrin (5-chloro-1,4-anhydroxylitol).

No amino derivatives of xylitol or xylitan are described in the literature. There is also little information on the amination of other polyhydric alcohols. 1,6-Diaminomannitol was prepared from dichlorodimethylene mannitol by heating the latter in an autoclave with ammonia in methyl alcohol [2].

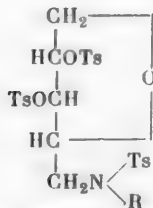
We studied the reaction of xylitan chlorohydrin with various amines and prepared the previously unknown compounds: 5-amino-1,4-anhydroxylitol (I), 5-ethylamino-1,4-anhydroxylitol (II), 5-diethylamino-1,4-anhydroxylitol (III), 5-phenylamino-1,4-anhydroxylitol (IV) and 5-piperidino-1,4-anhydroxylitol (V).

The amines were characterized as their tosyl derivatives, which we used for subsequent syntheses.

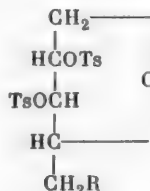


R = NH₂ (I), NHC₂H₅ (II), N(C₂H₅)₂ (III), NHC₆H₅ (IV), N(CH₂)₅ (V).

p-Toluenesulfonyl chloride reacted with the alcohol groups producing esterification (compounds VI-X) and also with the amino groups for the primary (I) and secondary (II and IV) amines, forming substituted sulfonamides (VI-VIII).



R = H (VI), C₂H₅ (VII), C₆H₅ (VIII).



R = N(C₂H₅)₂ (IX), N(CH₂)₅ (X),
Ts = O₂SC₆H₄CH₃.

*This article is the 7th in the series "Anhydrides and amino- and guanido-derivative of carbohydrates and polyhydric alcohols;" for the 6th report see J. Gen. Chem. 28, 3206 (1958) [preceding article].

TABLE 1

Preparation Conditions, Properties and Analyses of Xylitan Amino Derivatives

Exp. No.	Amino derivative	Reaction conditions	Yield (in %)	Melting point or boiling point	n_D^{20}	Found (in %)				Calculated (in %)			
						C	H	N	Cl	C	H	N	Cl
1	Aminoxylitan hydrochloride $C_8H_{12}O_3NCl$ (I)	100–110° 25 hours	37.3	133–134°	—	35.90, 36.03	7.43, 7.46	8.27, 8.34	21.11, 21.21	35.70	7.09	8.21	20.91
2	Ethylaminoxylitan $C_7H_{13}O_3N$ (II)	120° 72 hours	31.4	130 (1 mm)	1.4908	52.05, 52.40	9.51, 9.70	8.28, 8.51	—	52.15	9.38	8.69	—
3	Diethylaminoxylitan $C_9H_{19}O_3N$ (III)	120° 72 hours	51	127 (1 mm) 153–155 (5 mm)	1.4823	56.64, 56.69	10.43, 10.11	7.41, 7.47	—	57.12	10.11	7.40	—
4	Phenylaminoxylitan $C_{11}H_{15}O_3N$ (IV)	105° 20 hours	36	134–135	—	62.95, 63.25	7.58, 7.43	6.95, 7.08	—	63.23	7.52	6.69	—
5	Piperidinoxylitan $C_{10}H_{19}O_3N$ (V)	100° 17 hours	46	115–116	—	59.41, 59.58	9.48, 9.36	6.82, 6.80	—	59.85	9.47	6.93	—

TABLE 2

Tosyl Esters of Xylitan Amino Derivatives

Exp. No.	Tosyl derivatives	Melting point	Yield (in %)	Found (in %)				Calculated (in %)			
				C	H	N	S	C	H	N	S
1	(Ditosylxylitany)-toluenesulfonamide $C_{26}H_{30}O_6S_3N$ (VI)	146–147°	57.5	—	—	2.27, 2.50	15.60	—	—	2.35	16.15
2	(Ethyliditosylxylitany)-toluenesulfonamide (VII) $C_{28}H_{34}O_6S_3N$	120–121	50	—	—	2.27, 2.12	15.51, 15.28	—	—	2.24	15.40
3	Ditosyl ester of diethylaminoxylitan $C_{23}H_{32}O_7S_2N$ (IX)	154–155	61	55.48, 55.51	6.44, 6.19	2.39, 2.33	12.86, 12.77	55.40	6.47	2.81	12.85
4	(Phenyliditosylxylitany)-toluenesulfonamide $C_{32}H_{38}O_6S_3N$ (VIII)	141–142	87	—	—	1.93, 1.96	14.22, 14.62	—	—	2.09	14.32
5	Ditosyl ester of piperidinoxylitan $C_{34}H_{42}O_6S_3N$ (X)	130–132	41	—	—	—	12.33, 12.25	—	—	—	12.55

We are very grateful to Professor S. N. Danilov, under whose direction the work was performed.

EXPERIMENTAL

Amination of 5-chloro-1,4-anhydroxylitol. Crystalline xylitan chlorohydrin, synthesized by the method we described previously [1], was heated at 100-120° with excess ammonia or amine. We used 40% aqueous ammonia solution and freshly redistilled ethylamine, diethylamine, aniline and piperidine. In the first three cases, the experiments were performed in an autoclave and in the case of aniline and piperidine, in ampoules. The preparation conditions, properties and analyses of the amino derivatives are presented in Table 1. The amino-, ethylamino- and diethylaminoxylitans were sirupy products; the phenylamino- and piperidinoxylitans were crystalline substances.

The amines obtained were readily soluble in water, methyl and ethyl alcohols, acetone, dioxane, piperidine and amines, less soluble in chloroform and dichloroethane and soluble in benzene on heating; they were insoluble in ether.

The reactions gave a mixture of the amino derivative of xylitan and the original amine and their hydrochlorides. Since the properties of these compounds were different, it is better to describe the separation conditions and purification of the products for the separate cases.

Aminoxylitan (I). The reaction of xylitan chlorohydrin and ammonia yielded a homogeneous yellow solution from which the ammonia and water were distilled in vacuum. Absolute ethyl alcohol was added to the sirupy residue. After standing for a day, the solution deposited a crystalline precipitate, which was recrystallized 3 times from absolute ethyl alcohol to give aminoxylitan hydrochloride. Hydrogen chloride was passed through the filtrate after separation of the crystals to give an additional portion of the salt. Aminoxylitan (I) was isolated from the salt by treatment with soda in absolute methyl alcohol and formed a sirup, which could not be distilled in vacuum.

Diethylaminoxylitan (III). The reaction mixture after treatment of the chlorohydrin with diethylamine was diluted with dry dioxane and shaken on a mechanical shaker with alkali. The sirup left after evaporation of the dioxane was vacuum-distilled twice.

Ethylaminoxylitan (II). This product was isolated similarly to diethylaminoxylitan.

Phenylaminoxylitan (IV). When the dark-red homogeneous solution from the reaction with aniline was cooled, it was converted into a crystalline mass, mixed with tar. The crystalline part was filtered off and washed with dry ether. The ether-aniline solution gave a second portion of crystals. After isolation of the amino derivative from its salt with soda, the product was recrystallized three times from dichloroethane or chloroform.

Piperidinoxylitan (V). In the case of reaction with piperidine, the piperidine hydrochloride was filtered off from the reaction mixture after heating. Removal of the piperidine in vacuum left a mixture of piperidinoxylitan and its hydrochloride. The residue was recrystallized from benzene, treated with soda in dioxane and recrystallized twice from benzene, when it corresponded in analysis to piperidinoxylitan (V).

Tosylation of xylitan amino derivatives. The amino derivatives were tosylated by the usual method at room temperature in pyridine. In the cases of amino- and phenylaminoxylitan, the oil, precipitated on pouring the reaction mixture into ice water, crystallized rapidly. The crystals were carefully washed free from pyridine and recrystallized from ethyl alcohol. The properties and analyses are presented in Table 2.

In other cases, more complex treatment was required to obtain a crystalline product. Thus, in the case of diethylaminoxylitan, the oil was twice dissolved in methyl alcohol and precipitated with water, then extracted with chloroform, the solution dried over sodium sulfate, the chloroform distilled off and the residue crystallized on standing in a desiccator for two weeks. The ditosyl ester of diethylaminoxylitan was recrystallized from aqueous ethyl alcohol.

SUMMARY

1. A study was made of the reaction of 5-chloro-1,4-anhydroxylitol with ammonia, ethylamine, diethylamine, aniline and piperidine.

2. Previously unknown amino derivatives of xylitan and their tosylation products are described.

LITERATURE CITED

- [1] S. N. Danilov, A. N. Anikeeva, N. S. Tikhomirova-Sidorova and A. N. Shirshova, J. Gen. Chem. 27, 2434 (1957). *
- [2] W. Haworth, R. Heath and L. Wiggins, J. Chem. Soc. 1944, 155.

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A SEARCH FOR NEW METHODS OF SYNTHESIZING CELLULOSE ETHERS

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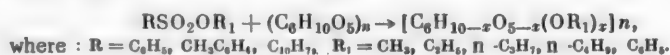
The preparation of partially substituted methyl and ethyl ethers of cellulose requires a high expenditure of dialkyl sulfates; in addition, dialkyl sulfates are noxious materials. In connection with this it seemed interesting to search for new alkylating agents which could be used for a substantial modification of the cellulose alkylation process.

It is known that esters of p-toluenesulfonic acid have a high reactivity, making it possible to use them for alkylating amines [1], mercaptans, thiophenols [2] and phenols [3].

The methyl and ethyl esters of p-toluenesulfonic acid were used for the alkylation of cellulose, but the properties of the cellulose ethers obtained were not described [4].

We investigated the possibility of alkylating cellulose both with esters of p-toluenesulfonic acid and with esters of toluenedisulfonic acid, benzenesulfonic acid and α -naphthylsulfonic acid.

Alkylation with these esters proceeds by the scheme



The alkylation was performed with alkali cellulose, cellulose, dissolved in 35.5% triethylbenzylammonium hydroxide, and hydrocellulose, dissolved in 9-10% sodium hydroxide.

Negative results were obtained in all cases in the alkylation of alkali cellulose. The alkylation of cellulose, dissolved in the organic base, proceeded more rapidly than with solutions in alkali; thus, with an alkylation in alkali solution, it was only possible to introduce 3-10% of methyl or ethyl residues, while with an alkylation in an organic base solution, the content of residues reached 12 to 35%. In the alkylation of cellulose in alkali solution with esters of benzenesulfonic acid, it was found that the methyl ester reacted more readily than the ethyl and the ethyl more readily than the propyl, etc.

On the basis of the experimental material, the esters of benzenesulfonic acid may be arranged in the following series according to the ease of their substitution reactions:



We were unable to obtain such a series for the same esters in the alkylation of cellulose in the organic base solution, as the reaction proceeded more vigorously.

A comparison of the substitution capacity of the ethyl ester of p-toluenesulfonic acid with the diethyl ester of toluenedisulfonic acid in the etherification of cellulose in an organic base showed that the monoester was more reactive than the diester.

EXPERIMENTAL

(With the participation of F. G. Khavgina)

The esters of the sulfonic acids were prepared from the acid chlorides of the sulfonic acids and alcohols by the method of Izmail'skii and Razorenov [3], with the exception of the phenyl ester of benzenesulfonic acid, which was prepared by heating equimolecular amounts of sodium phenolate and benzenesulfonyl chloride in a

TABLE 1

Alkylation of 2.5% Hydrocellulose Solution (Cu number, 9.3) in 9.50% NaOH Solution with a Molecular Ratio of Ester to Cellulose of 6:1

Exp. No.	Alkylating reagent	Reaction temperature	Time (in hours)	OCH ₃ , OC ₂ H ₅ (in %)	Degree of substitution	Ester recovered (moles)
1	C ₆ H ₅ SO ₂ OCH ₃	18-20°	2.0	1.47	0.09	4.31
2		30 ± 2	2.0	3.71	0.24	3.65
3		50 ± 2	2.0	10.55	0.69	—
4	C ₆ H ₅ SO ₂ OC ₂ H ₅	50 ± 2	2.0	2.95	0.16	2.50
5		70 ± 2	2.0	7.81	0.40	—
6	C ₆ H ₅ SO ₂ n-OC ₃ H ₇	50 ± 2	2.0	None	None	4.55
7	C ₆ H ₅ SO ₂ n-OC ₄ H ₉	70 ± 2	2.0	None	None	3.91
8	CH ₃ C ₆ H ₄ SO ₂ OCH ₃	50 ± 2	4.0	8.09	0.53	—
9		70 ± 2	4.0	5.95	0.40	—
10	CH ₃ C ₆ H ₄ SO ₂ OC ₂ H ₅	50 ± 2	4.0	Traces	None	4.62
11		70 ± 2	4.0	7.76	0.41	Traces
12	C ₁₀ H ₇ SO ₂ OC ₂ H ₅	70 ± 2	2.0	Traces	None	4.77

TABLE 2

Alkylation of 2.5% Cellulose Solution in 35.5% Organic Base Solution with a Molecular Ratio of Ester to Cellulose of 6:1

Exp. No.	Alkylating reagent	Reaction temperature	Time (in hours)	OCH ₃ , OC ₂ H ₅ (in %)	Degree of substitution
1	C ₆ H ₅ SO ₂ OCH ₃	55-60°	0.5	16.93	1.11
2	C ₆ H ₅ SO ₂ OC ₂ H ₅	50 ± 2	3.0	35.30	1.89
3	C ₆ H ₅ SO ₂ n-OC ₃ H ₇	50 ± 2	1.0	—	1.13
4	C ₆ H ₅ SO ₂ n-OC ₄ H ₉	50 ± 2	2.0	—	1.11
5	CH ₃ C ₆ H ₄ SO ₂ OCH ₃	50 ± 2	3.0	21.50	1.41
6	CH ₃ C ₆ H ₄ SO ₂ OC ₂ H ₅	50-60	3.0	34.36	1.85
7		70-80	3.0	33.34	1.80
8	CH ₃ C ₆ H ₃ (SO ₂ OC ₂ H ₅) ₂	50-55	4.0	Traces	None
9	C ₁₀ H ₇ SO ₂ OC ₂ H ₅	65-70	4.0	12.61	0.67
10	C ₁₀ H ₇ SO ₂ OC ₂ H ₅	18-20	1.0	23.19	1.24

benzene medium at 35-40° for 8 hours. The sulfonic esters obtained were used for the synthesis of cellulose ethers. In the first series of experiments the cellulose was alkylated in 9.5% sodium hydroxide solution. First of all, samples of hydrocellulose were prepared by solution in 85% phosphoric acid [5]. The moist hydrocellulose (Cu number, 9.3) was dissolved in 9.5% sodium hydroxide at room temperature, then the solution was heated to 30, 50 and 70°, 6 moles of the alkylating reagent added and the reaction performed for 1-4 hours (Table 1).

In the second series of experiments, the alkylation was performed in a 35.5% solution of triethylbenzylammonium hydroxide. The cellulose was dissolved in the organic base at room temperature, then the solution heated to 50-80° and 6 moles of alkylating reagent added to it; the reaction proceeded for 0.5-4 hours (Table 2). At the end of the reaction in both the first and the second series of experiments, the unreacted ester was isolated by ether extraction and the unreacted portion determined (Table 1). The aqueous layer was heated to boiling and this coagulated the cellulose ether, which was purified by the usual method.

The cellulose ethers obtained in the first series of experiments were in the form of powders, while the second method gave cellulose ethers as a flocculent mass.

A comparison of experiments 3, 5 and 7 (Table 1) shows that under the same conditions, the alkylating capacity of esters of benzenesulfonic acid falls with an increase in the alkyl radical and similarly for the esters of p-toluenesulfonic acid as shown in experiments 9 and 11.

The alkylation of cellulose in alkali solution gave a methylcellulose (Exp. 3, Table 1), which dissolved in 2-4% sodium hydroxide solution giving a low-viscosity, clear solution.

The data in Table 2 show that in the alkylation of cellulose in the organic base, all the alkylating reagents, with the exception of diethyl toluenedisulfonate, rapidly form cellulose ethers. In experiments 1, 5 and 10 (Table 2), we obtained water-soluble methyl and ethyl ethers of cellulose, which gave very viscous, clear solutions. The propyl and butyl ethers of cellulose only swelled in an alcohol-benzene solution.

Comparison of the experiments performed under the same conditions (Tables 1 and 2) shows that in the organic base solution the alkylation proceeds more completely than in the alkali solution, which is caused by the different natures of sodium hydroxide and the organic base.

SUMMARY

1. Cellulose was alkylated in solutions of alkali and an organic base with the methyl and ethyl esters of p-toluenesulfonic acid, the diethyl ester of toluenedisulfonic acid, the methyl, ethyl, n-propyl and n-butyl esters of benzenesulfonic acid and the methyl and ethyl esters of α -naphthalenesulfonic acid.
2. The medium was shown to have an effect on the transfer of the radical in the etherification of cellulose in solution.
3. It was established that in an alkali solution the ease of alkylation with benzenesulfonic esters fell from methyl to ethyl to n-propyl, etc.
4. It was found that the introduction of a second alkyl group into the monoester of toluenesulfonic acid considerably lowered the capacity of the ester to alkylate cellulose.

LITERATURE CITED

- [1] J. Fern and A. Lapworth, J. Chem. Soc. 101, 273 (1912).
- [2] A. Shirley and H. Reedy, J. Am. Chem. Soc. 73, 4885 (1951).
- [3] V. A. Izmail'skii and B. A. Razorenov, J. Russ. Chem. Soc. 52, 359 (1920).
- [4] J. W. Weaver, C. A. Mackenzie and A. Shirley, Ind. Eng. Chem. 46, 1490 (1954).
- [5] A. B. Davankov, Laboratory Work on the Chemistry of Cellulose and Cellulose Films, 67 (1939).*

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COMPARATIVE DISTRIBUTION OF CARBON DISULFIDE IN THE MAIN AND SIDE REACTIONS IN THE PREPARATION OF VISCOSE AT LOW TEMPERATURE AND UNDER NORMAL CONDITIONS

E. A. Abramova

Many publications have pointed out the relation between the physicochemical properties of viscose fibers, the degree of substitution of the xanthate and the uniformity of distribution of the ester groups along the chain [1]. The greater the number of ester groups in the xanthate and the higher the uniformity of their distribution, the more homogeneous is the structure of the fibers.

TABLE 1

Amount of carbon disulfide added (in %)	Low temperature conditions (°)	Normal temperature conditions (°)
15	27—28	—
20	35	30
30	40—41	35—36
38	58—62	46—48
40	65—66	50—52

Our previous work [2, 3] showed that viscose formation under low-temperature conditions gave a more advantageous distribution of carbon disulfide as regards ester formation with a low consumption of carbon disulfide.

In the present work an examination was made of the comparative distribution of carbon disulfide at two temperatures (low temperature and that normally used) with 15, 20, 30, 38 and 40% of carbon disulfide used. All the experiments were performed on one sample of original cellulose.

(Under low temperature conditions, the alkali cellulose preparation and one third of the sulfidation time was at a temperature of 0 to +5°. The xanthated fibers were dissolved at -5 to -7°.

Under normal conditions, the viscose is formed at from +15 to +30°). The solutions obtained were analyzed for composition, degree of substitution (γ) and the distribution of carbon disulfide between the main and the side reactions. The amount of sulfur in the ester groups and in the side products was determined by decomposition with acid and, in parallel, the degree of substitution of the xanthate was determined by iodometric titration. The sodium sulfide was determined potentiometrically.

Investigations were made on viscose solutions with practically the same α -cellulose content and with various free alkali contents. The tables give only the basic data, established in many experiments.

Table 1 gives the degree of substitution (γ is the number of hydroxyl groups in 100 elementary units of the cellulose macromolecule, substituted with ester groups) of the xanthate in the viscose solutions obtained, with a total alkalinity of 7.1-7.3%

Table 1 shows that in viscose formation at low temperatures with the same amounts of carbon disulfide added, esters with higher degrees of substitution were obtained.

Table 2 gives data on the distribution of xanthate sulfur and side-product sulfur for the two viscose formation conditions with the same viscose solutions. The difference in the distribution values is very clear; moreover, the lower the amount of carbon disulfide introduced into the reaction, the more advantageous is the distribution.

If the concentration of alkali in the viscose is not 7.1-7.3%, as in experiments in Tables 1 and 2, but only 5-6%, then the reduction in the free alkali in the viscose solution has a considerable effect on carbon disulfide distribution, increasing the degree of esterification of the xanthate. The corresponding data are given in Table 3.

TABLE 2

Amount of carbon disulfide added (in %)	Distribution of S (in %)			
	xanthate S	side product S	xanthate S	side product S
	Low temperature conditions		Normal conditions	
15	88	12	—	—
20	82	18	—	—
30	79	21	74	26
38	77	23	64	36
40	76	24	61	39

TABLE 3

Amount of carbon disulfide added (in %)	Distribution of S (in %)		γ	Distribution of S (in %)		γ
	xanthate S	side product S		xanthate S	side product S	
	Low temperature conditions			Normal conditions		
15	87	13	28	—	—	—
30	85	15	44	—	—	—
38	82	18	65	68	32	54
40	79	21	80	66	34	55

TABLE 4

Amount of carbon disulfide added (in %)	Distribution of S (in %)		γ	Distribution of S (in %)		γ
	xanthate S	side product S		xanthate S	side product S	
	Low temperature conditions			Normal conditions		
15	76	24	26	—	—	—
20	77	23	32	72	28	26
30	75	25	34	69	31	31
38	71	29	52	67	33	48
40	70	30	62	66	34	50

The alkali concentration is of great importance in the low temperature process. The water, which is present as ice crystals in capillary spaces in the cellulose fiber, acts as a conductor, when the system thaws out, for the alkaline solution into the newly formed fissures—the intermolecular spaces broadened by the ice. It is possible that with a fall in the alkalinity of the viscose solutions, there is further esterification of the hydroxyl groups which become available due to the larger amount of frozen, and then thawed, water.

We also performed experiments without cooling the alkali cellulose before sulfidation as specified for the low-temperature conditions. By preparing the alkali cellulose at a temperature of 0 to +2° and cooling it to the same temperature before sulfidation, it is possible to improve considerably the swelling and activation of the cellulose. We should also note that at the beginning of sulfidation at these temperatures there was a considerable decrease in the formation of viscose antistabilizers. With low temperature solution, the dispersion of the xanthated fibers was improved.

Table 4 shows data on the distribution of carbon disulfide between the main and the side reactions under the two sets of conditions without the cooling of the alkali cellulose and the initial low-temperature sulfidation, for viscoses with a total alkali content of 7-7.1%.

Excluding the cooling of the alkali cellulose and the low-temperature sulfidation had a considerable effect on the distribution of carbon disulfide and, consequently, on the degree of substitution of the xanthate, which was decreased. However, the effect of low temperature solution was clearly marked.

Using low temperature conditions, it is possible to prepare stable viscoses by dissolving xanthated fiber in water. The viscose solutions obtained have a satisfactory degree of substitution, good viscosity curves with a minimum after 15-20 hours and a high degree of purity (according to comparative photometry).

It is not advantageous to reduce the total alkalinity of the viscose solutions below 4.5-5% as at lower alkali concentrations, hydrolysis of the xanthate ester is accelerated and the sulfur distribution is displaced towards the formation of side products.

SUMMARY

1. When the general method of cellulose activation by low temperatures is used for viscose formation, the reaction equilibria are displaced towards the formation of cellulose xanthate.
2. Using low-temperature conditions and from 15 to 40% of carbon disulfide, it is possible to prepare xanthates with a degree of substitution of from 25 to 80, when under normal conditions the degree of xanthation is from 35 to 50.
3. With a decrease in the alkalinity of the viscose solutions, the distribution of carbon disulfide between the main and the side reactions is displaced towards the formation of cellulose ester.

LITERATURE CITED

- [1] W. Schramek, *Cellulosechemie*, 20, 138 (1942); H. Klare, *Faserforsch und Textiltechnik*, 7, No. 5 199 (1956).
- [2] N. I. Nikitin and E. A. Abramova, *J. Appl. Chem.* 28, 253 (1956).*
- [3] E. A. Abramova, *J. Appl. Chem.* 28, 384 (1956).*

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INVESTIGATIONS IN THE FIELD OF CONJUGATED SYSTEMS

XCV. REACTIONS OF PIPERYLENE WITH ITS HYDROCHLORIDE AND WITH THE 1,4-HYDROCHLORIDE OF ISOPRENE*

A. A. Petrov, N. A. Razumova and M. L. Genusov

In previous communications it was shown that various unsaturated chlorides of the allyl type react with diene hydrocarbons in the presence of SnCl_4 and ZnCl_2 to form mixtures of telomers [1]. The amount of products of simple addition of the halogen derivatives to the dienes (in the ratio 1:1) in this mixture depended, in the first instance, on the nature of the halogen derivative and the direction of the addition was determined by the structure of the diene hydrocarbon.

In the present work, this rule was confirmed on new examples. The reaction of piperylene with its hydrochloride (2-chloropentene-3) could be readily stopped at the formation of the substance $\text{C}_8\text{H}_{12}-\text{C}_8\text{H}_9\text{Cl}$, while in the reaction of the same diene with an isomeric chloride, the 1,4-hydrochloride of isoprene (1-chloro-3-methylbutene-2), considerably larger amounts of higher telomers were formed under the same conditions. In both cases, the ratio between the simple adducts and the higher telomers depends on the extent of telomerization.

Thus, it was established that with primary halogen derivatives of the allyl type there is a greater degree of telomerization than with secondary derivatives.

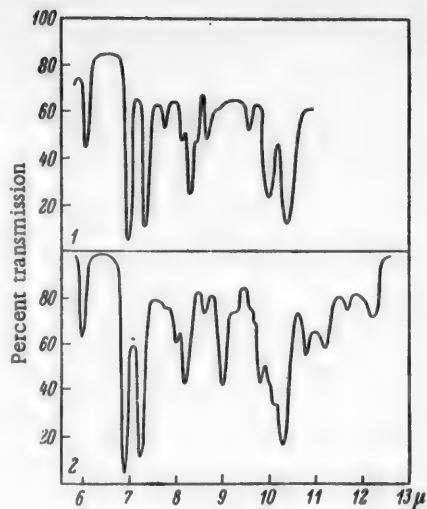
As a result of adding 2-chloropentene-3 to piperylene with a degree of telomerization of the order of 35-70%, we obtained predominantly a substance which distilled in vacuum over a 1° range. The amount of higher telomers was 15-35% of the total mixture.

The structure of the constant-boiling substance referred to above was established in the following way.

1. According to analysis data it had the formula $\text{C}_{10}\text{H}_{17}\text{Cl}$ and contained not less than 90% of diene (Kaufman's method) and a readily hydrolyzable chlorine atom.
2. In ozonolysis it gave acetic, α -chloropropionic and methylsuccinic acids. The latter was isolated in about 80% yield.
3. When hydrogenated over Pd/CaCO_3 it formed 4-methylnonane.
4. It underwent the Sommelet reaction to the extent of 12% after 6 hours and 25% after 100 hours. The residue after the Sommelet reaction had the properties of the original chloride. After a further treatment with urotropine for 100 hours, the material did not change its properties also and over 6 hours, it reacted further with urotropine (in an analytical determination) to the extent of 11%. These data indicate the relative individuality of the product.

As a result of the Sommelet reaction, we obtained a carbonyl compound in a total yield of 5.4% on the chloride taken and 24% on that reacted. The substance had an unpleasant, obtrusive smell. Its infrared spectrum showed bands characteristic of conjugated double bonds (1632 cm^{-1}), the group $-\text{CH}=\text{CH}-$ (973 cm^{-1}) and a conjugated carbonyl group (1688 cm^{-1}). In the region of 2730 cm^{-1} , the substance absorbed very weakly, indicating that aldehydes were absent or only present in insignificant amounts.

*Diene compounds. LXXI. Reactions of Dienes with Halogen Derivatives. VII.

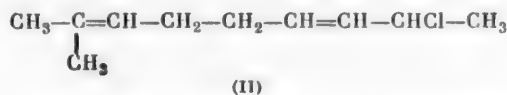


Infrared absorption spectra of telomerization products of 2-chloropentene-3 (1) and 1-chloro-3-methylbutene-2 (2) with piperylene.

discrete substances by distillation. To establish the structure of the main substance, we worked with a fraction boiling over a range of 10° . We thus obtained the following data.

1) The mixture investigated had the composition $C_{10}H_{17}Cl$ and did not contain less than 80% of a diene halogen derivative (Kaufman's method). About 90% of the chlorine was readily hydrolyzable. 2) During ozonolysis it formed acetone and α -chloropropionic and succinic acids. 3) On hydrogenation over $Pd/CaCO_3$ it gave a hydrocarbon with a boiling point close to that of 2-methylnonane, but slightly higher specific gravity and refractive index. 4) In the Sommelet reaction, 23% of the material reacted after 100 hours. 5) The infrared spectrum showed a double-bond frequency of 1670 cm^{-1} , the frequency of the group $-CH=CH-$ at 970 cm^{-1} and the frequency of the group $C=CH-$ at 822 cm^{-1} (all of high intensity). The spectrum also showed the frequencies of a vinyl group ($929, 990$ and 6100 cm^{-1}), but they were weak (figure).

These data indicate that the main component of the chlorides investigated may be represented by the formula of 8-chloro-2-methylnonadiene-2,6 (II).



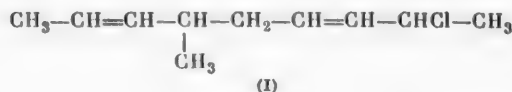
Thus, like the hydrochloride of piperylene, the hydrochloride of isoprene adds to piperylene predominantly in the 1,4-position. The nature of the impurity containing a vinyl group requires an independent study. We cannot exclude the possibility of addition at the double bond of the allyl isomer of the hydrochloride (dimethylvinylchloromethane). It is also possible that the impurities are products from decomposition during distillation of the dimers of the halogen derivative or higher telomers.

EXPERIMENTAL

Reaction of piperylene with its hydrochloride. To a solution of piperylene and its hydrochloride (0.6 mole of each) in 30 ml of methylene chloride was added 2 ml of a 5% solution of SnCl_4 in the same solvent. The mixture was stirred at $10-15^\circ$ until the specific gravity increased by 0.044 and then the reaction was stopped by the addition of diethylamine. Distillation of the reaction mixture in vacuum gave 35 g of telomers, which corresponded to 32% telomerization. The telomers were separated by distillation into a first fraction (27 g) and higher telomers (7 g). The ratio between these products was 4:1;

5. The infrared spectrum of the chloride investigated had intense frequencies of the group $-CH=CH-$ (1660 and 965 cm^{-1}) but did not contain the frequencies of the vinyl group ($920, 980$ and about 6100 cm^{-1}).

All these data indicate that the main addition product (more than 80%) of 2-chloropentene-3 to piperylene is 2-chloro-6-methylnonadiene-3,7 (I).



It was thus established that piperylene adds its hydrochloride in the 1,4-positions, i.e., in the same way as hydrogen halides. The particular tendency of piperylene for 1,4-addition is apparently due to its high polarity (dipole moment 0.68 D).

In the reaction of piperylene with the 1,4-hydrochloride of isoprene (prenyl chloride) with telomerization to the extent of about 75%, we obtained very little of the primary telomerization products. With about 25% telomerization, the yield of the latter was raised to 40% of the total telomer mixture, but we were unable to isolate

In a second experiment with the same amounts of starting materials, the increase in specific gravity was 0.062. We obtained 58 g of telomers. The degree of telomerization was of the order of 55%. The ratio between the first fraction and the higher telomers was 2:1.

Finally, in a third experiment the degree of telomerization was of the order of 65% and this ratio was 1.2:1.

When the first fraction was distilled through a Widmer fractionating column, more than 90% of it passed over at a constant temperature. For this portion we found:

B.p. 78.5° (10 mm), d_4^{20} 0.8928, n_D^{20} 1.4624, M_{rD} 53.22; calc. 52.31.
Found % C 69.74; 69.67; H 10.12, 10.04; Cl 20.15. $C_{10}H_{17}Cl$. Calculated % C 69.55; H 9.92; Cl 20.53.

Infrared spectrum: 965 v.s., 1007 s., 1056 med., 1152 med., 1188 med., 1212 s., 1238 med., 1293 med., 1369 v.s., 1440 v.s., 1660 med and 1765 med., cm^{-1} .

A 92% diene content was found by Kaufman's method. When a sample of the substance was boiled in an aqueous alcohol solution for 2 hours, 98% of the chlorine passed into solution.

5 g of the chloride was taken for ozonization. The normal treatment of the ozonides gave acetic acid (b.p. 40-45° at 50 mm), α -chloropropionic acid (b.p. 75-80° at 5 mm, n_D^{20} 1.4350 and an anilide with m.p. 93°, which corresponds to literature data [3]) and 3 g of methylsuccinic acid (m.p. 108°, mixed melting point 108°).

For hydrogenation we used 15.8 g of the substance and 40 g of Pd/CaCO₃ in 120 ml of methyl alcohol. 4885 ml of H₂ (765 mm, 21.5°) was absorbed, corresponding to 71.4%. The hydrogenation products were separated by diluting the distillate from steam distillation with a saturated solution of CaCl₂. We obtained 7.5 g of hydrocarbon (fraction with b.p. 165-170°) and 2.6 g of residue. A second distillation of this fraction yielded 4-methylnonane with the following constants:

B.p. 165-166°, d_4^{20} 0.7360, n_D^{20} 1.4140. These data are close to those reported in the literature [4].

When 52.5 g of the substance was shaken for 100 hours with urotropine by Sommelet's method, we obtained a total of 2.5 g of carbonyl compounds with b.p. about 93° (10 mm), d_4^{20} 0.8724 and n_D^{20} 1.4670.

Found % C 77.70, 77.52; H 10.80, 10.79. $C_{10}H_{16}O$. Calculated % C 78.90; H 10.60.

The analytical data show that the substance was not completely pure.

Infrared spectrum: 925 w., 973 v.s., 1020 v.w., 1039 v.w., 1100 v.w., 1150 v.w., 1174 w., 1258 v.s., 1369 v.s., 1465, 1465 v.s., 1632 med., 1688 v.s., 2730 w., 2852 w., 2869 s., 2914 v.s., 2955 v.s., and 3022 w., cm^{-1} .

The 2,4-dinitrophenylhydrazone was red and had m.p. 72-73° (from alcohol).

Found % N 17.18. $C_{16}H_{22}O_4N_4$. Calculated % N 16.76.

The residue after the Sommelet reaction (40.5 g, 77%) was the original chloride.

B.p. 78.5° (10 mm), d_4^{20} 0.8917, n_D^{20} 1.4624.

Found % C 69.55, 69.45; H 9.72, 9.92; Cl 20.62. $C_{10}H_{17}Cl$. Calculated % C 69.55; H 9.92; Cl 20.53.

After a further 100 hours treatment by the Sommelet method, the residue was shown to contain 10.9 and 11.0% of reactive chlorides by an analytical method [2] over 6 hours.

Reaction of piperylene with prenyl chloride. Under the usual conditions and with an increase in specific gravity of 0.035 (about 35% telomerization), 41 g of prenyl chloride and 28 g of piperylene in 40 ml of methylene chloride yielded 24.5 g of a mixture of telomers, which was separated by distillation (5 mm) into a fraction boiling up to 100° (10.5 g) and higher telomers (13 g). The ratio between these products was 1:1.25.

With the same amount of starting materials and an increase in the specific gravity of 0.072, we obtained 54 g of telomers. The degree of telomerization was about 75%. Distillation yielded 6.5 g of a fraction with b.p. up to 100° (5 mm) and 47 g of residue. The ratio between these products was 1:7.

In a second distillation of the fraction with b.p. up to 100° (5 mm), the bulk of it (more than 60%) passed over in a 10° range. For this part we found:

b.p. 75-85° (10 mm), d_4^{20} 0.9152, n_D^{20} 1.4712 M_R^D 52.73; calc. 52.31.
Found % C 69.57, 69.48; H 9.88, 9.45; Cl 20.55, 20.41. $C_{10}H_{17}Cl$. Calculated % C 69.55; H 9.22; Cl 20.53.

Infrared spectrum: 762 v.w., 822 med., 858 w., 893 med., 929 med., 970 v.s., 990 w., 1018 med., 1076 w., 1114 s., 1166 w., 1219 s., 1247 w., 1382 v.s., 1456 v.s., and 1670 s., cm^{-1} .

Kaufman's method indicated an 80% diene content. The Sommelet - Leets method [2] showed a 23% active chloride content (shaking for 100 hours).

Ozonolysis of the substance (5 g) yielded acetone (2, 4-dinitrophenylhydrazone - m.p. 125°, mixed melting point - same temperature), liquids containing chloroacids with b.p. 75-85° (9 mm) - predominantly α -chloropropionic acid (anilide - m.p. 93°) and succinic acid with m.p. 183° (a mixed sample melted at the same temperature).

In the hydrogenation of 9.5 g of the substance over 35 g of Pd/CaCO₃, 2810 ml of H₂ (748 mm, 20°) was absorbed, which corresponds to 68%. Steam distillation of the reaction mixture, salting-out with CaCl₂ and subsequent distillation yielded 3 g of hydrocarbon with b.p. 165-167°, d_4^{20} 0.7490 and n_D^{20} 1.4190. For 2-methylnonane, the literature reports the constants [4]: b.p. 167.8°, d_4^{20} 0.7334, n_D^{20} 1.4125.

SUMMARY

1. An investigation was made of the telomerization of piperylene with its hydrochloride (2-chloropentene-3) and the 1,4-hydrochloride of isoprene - (1-chloro-3-methylbutene-2).
2. It was shown that in the first case the products of 1:1 addition were obtained in considerably greater yield than in the second. In both cases the yields depended strongly on the degree of telomerization.
3. The structures of the first addition products (in the ratio 1:1) were established from data on their ozonization, hydrogenation and reactions with urotropine (Sommelet) and also from a study of their infrared spectra.
4. It was shown that in both cases addition of the halogen derivative in the 1,4-position predominated.

LITERATURE CITED

- [1] A. A. Petrov et al., J. Gen. Chem. 28, 1128, 1435, 2138 (1958).*
- [2] K. V. Leets, A. I. Piliavskaia and M. I. Korovkina, J. Gen. Chem. 27, 2969 (1957).*
- [3] R. Shriner and R. Fuson, Systematic Qualitative Analysis of Organic Compounds. For. Lit. Press, 217 [Russian translation] (1950).
- [4] R. D. Obolentsev, Physical Constants of Hydrocarbons. State Fuel Tech. Press (1953)[In Russian].

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CHEMICAL CONVERSIONS OF α -HALO KETONES.

VI. THE ACTION OF SODIUM PHENOLATE AND CRESOLATE ON α -BROMOCYCLOHEXANONE

T. I. Temnikova and N. A. Oshueva

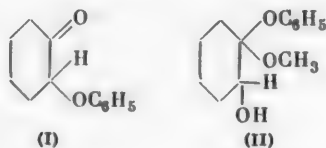
In previous work [1] it was shown that the action of sodium phenolate on aliphatic-aromatic α -bromo ketones yielded different reaction products, depending on the solvent: if the reaction was performed in acetone or ether, α -phenoxy ketones were formed; if the solvent used was methyl alcohol, we obtained the methyl phenyl ketal of the keto alcohol, corresponding to the bromo ketone used. In the latter case, the α -phenoxy oxide (phenyllactolide of the α -keto alcohol) was formed as an intermediate product; however, despite conclusive evidence of its presence in the solution, it was not possible to isolate it in a pure form [2].

In this work, a study was made of the reaction of sodium phenolate and p-cresolate with α -bromocyclohexanone in methyl alcohol; it seemed interesting to determine whether the formation of mixed ketals would be observed in the cyclohexane series; the formation of these would provide indirect evidence of the intermediate formation of phenyllactolides in this series.

The action of sodium phenolate on α -bromocyclohexanone was first studied in petroleum ether by F. Ebel [3]. In a rapid treatment of the reaction products, he isolated a substance with m.p. 64-65° with the composition $C_{12}H_{14}O_2$. At first Ebel assigned to this the formula of phenoxy cyclohexanone; however, having found that the phenoxy group was removed very readily for phenoxy ketones by the action of phenylhydrazine (forming the phenylosazone of cyclohexanolone), indicating a phenoxy oxide, he proposed that the latter was cleaved hydrolytically under the conditions of the reaction with phenylhydrazine to form a keto alcohol. We should, however, note that somewhat earlier, Kötze, in working with α -methoxy- and α -ethoxycyclohexanone, had noted the ease of removal of the alkoxy group under the action of phenylhydrazine [4]. In 1948 the work of Mousseron appeared, in which he prepared authentic phenoxy cyclohexanone by oxidation of the monophenyl ether of cyclohexanediol-1,2. The substance melted at 65° [5], like the compound of Ebel; however, the identity of the two substances, melting at the same temperature but prepared by different methods, was not proved.

In the present investigation, we again prepared the substance by Ebel's method, with the difference that the sodium bromide was separated by centrifuging and not washed out with water, to prevent decomposition of the phenyllactolide, if it were obtained. The substance obtained, which had m.p. 65°, was examined spectrochemically. The infrared spectrum showed absorption at 1730 cm^{-1} (carbonyl) and at 1588 cm^{-1} (phenyl). It was thus confirmed that α -phenoxy cyclohexanone (I) was formed under Ebel's conditions (petroleum ether as solvent). The phenoxy cyclohexanone was characterized as the 2,4-dinitrophenylhydrazone. While phenylhydrazine removed the phenoxy group when the phenoxy ketone was heated with phenylhydrazine in acetic acid to give the phenylosazone, 2,4-dinitrophenylhydrazine in sulfuric acid reacted with the carbonyl group only. Separate experiments showed that the phenoxy ketone was stable in hot acetic acid solution (95%) and was not hydrolyzed.

Treatment of α -bromocyclohexanone in methyl alcohol with sodium phenolate gave the methyl phenyl ketal of cyclohexanolone (II).



Immediately after vacuum-distillation, the methyl phenyl ketal appeared as a colorless, immobile liquid with a sharp, characteristic smell, slightly reminiscent of the smell of phenol (it did not give a reaction for free phenol with FeCl_3). The substance was very unstable; under prolonged heating in vacuum it partly decomposed, therefore, for isolation in an analytically pure state, the ketal was rapidly distilled in small portions; even after a few hours in the cold the liquid acquired a pink color, which gradually became dark-yellow and when a sample was treated with ferric chloride, it gave a violet color.

In contrast to the aliphatic-aromatic methyl phenyl ketals, the freshly distilled ketal (II) reduced Fehlings solution on heating, apparently due to ready hydrolysis. The substance was hydrolyzed rapidly when heated with a 5% aqueous alcohol solution of sulfuric acid; the hydrolysis products, phenol and cyclohexanolone, were characterized as triiodophenol and the 2,4-dinitrophenylsazone. We should note that the reaction with 2,4-dinitrophenylhydrazine proceeded rapidly and almost quantitatively; this derivative is better for characterization of cyclohexanolone.

Treatment of α -bromocyclohexanone with sodium p-cresolate in methyl alcohol also gave the methyl p-cresyl ketal of cyclohexanolone. This ketal was also unstable.

The high instability of the methyl phenyl ketal of cyclohexanolone differed sharply from the stability of methyl phenyl ketals of α -keto alcohols of the aliphatic-aromatic series; the latter are crystalline substances, which are stable to storage and not hydrolyzed when heated with Fehling's solution.

EXPERIMENTAL

α -Bromocyclohexanone was prepared by the method of L. A. Ianovskaia and A. P. Terent'ev [6]. The b.p. was 83-86° at 10 mm.*

Preparation of methyl phenyl ketal of cyclohexanolone. 11.2 g of α -bromocyclohexanone was gradually added to a solution of sodium phenolate, prepared from 2.7 g of sodium, 11 g of phenol and 60 ml of methyl alcohol. A precipitate of sodium bromide began to form immediately. Next day the precipitate was separated, the methyl alcohol removed in vacuum and the viscous orange residue freed from residual sodium bromide. Crystallization did not occur, even after long storage. Two vacuum distillations yielded 6 g of ketal with b.p. 70-72° at 5 mm, d_4^{20} 1.089, n_D^{20} 1.5100.

Found %: C 70.28, 69.85; H 8.6, 8.05; OCH_3 14.45, 14.40. M 236. $\text{C}_{13}\text{H}_{18}\text{O}_3$. Calculated %: C 70.27; H 8.10; OCH_3 13.97. M 222.

The methyl phenyl ketal of cyclohexanolone was hydrolyzed by heating for 2 hours with a 5% aqueous alcohol solution of sulfuric acid. The hydrolysis product was made alkaline and extracted with ether in an extractor. After evaporation of the ether, the residue partially crystallized. The whole oily reaction product was treated with a sulfuric acid solution of 2,4-dinitrophenylhydrazine. A voluminous, bright-red precipitate of the 2,4-dinitrophenylsazone of cyclohexanolone formed. The m.p. was 224-225°. A mixture with an authentic sample melted at the same temperature.

Found %: N 23.53. $\text{C}_{18}\text{H}_{16}\text{O}_8\text{N}_8$. Calculated %: N 23.72.

Preparation of methyl p-cresyl ketal of cyclohexanolone. 24 g of bromo ketone was added to a solution of sodium p-cresolate, prepared from 3.3 g of Na, 15.3 g of p-cresol and 55 ml of methyl alcohol. The reaction mixture was treated in the usual way, the ether solution washed with alkali and the product vacuum-distilled twice to give a substance with b.p. 90° at 10 mm, n_D^{20} 1.5005; d_4^{20} 1.061.

Found %: C 71.08, 71.20; H 8.34, 8.46; OCH_3 12.75. $\text{C}_{14}\text{H}_{20}\text{O}_3$. Calculated %: C 71.18; H 8.47; OCH_3 13.13.

Preparation of 2,4-dinitrophenylhydrazone of α -phenoxycyclohexanone. The α -phenoxy ketone was prepared by Ebel's method. A hot alcohol solution of the phenoxy ketone was added to an alcohol-sulfuric acid solution of 2,4-dinitrophenylhydrazine; the 2,4-dinitrophenylhydrazone began to precipitate immediately. The product was recrystallized from ethyl alcohol. The m.p. was 149-150°.

*Note added during proofreading. All our experimental data show that despite the statement of I. V. Machinskaja and A. S. Podberezina [J. Gen. Chem. 28, 1501 (1958)], α -bromocyclohexanone may be prepared in good yield by the method of Ianovskaia and Terent'ev.

Found %: N 15.23, 15.44. $C_{15}H_{15}O_5N_4$. Calculated %: N 15.14

SUMMARY

Treatment of α -bromocyclohexanone with sodium phenolate and p-cresolate in methyl alcohol gave methyl phenyl and methyl cresyl ketals of cyclohexanone.

LITERATURE CITED

- [1] T. I. Temnikova and S. Mikhurdari, J. Gen. Chem. 24, 1819 (1954);* G. A. Ugol'nikova, J. Gen. Chem. 27, 343 (1957);* T. I. Temnikova, G. A. Ugol'nikova, O. A. Netsetskaya and T. B. Remizova, J. Gen. Chem. 27, 2491 (1957).*
- [2] G. A. Ugol'nikova, Bull. Leningrad State University, Phys. and Chem. Series, No. 10, 106 (1957).
- [3] F. Ebel, Helv. Chim. Acta, 12, 1 (1929).
- [4] A. Kötze, K. Blendersmann, R. Rosebusch and E. Siringhaus, Lieb. Ann. 400, 64 (1913).
- [5] M. Mousseron and R. Jacquier, C. r. 229, 374 (1949).
- [6] L. A. Ivanovskaya and A. P. Terent'ev, J. Gen. Chem. 22, 1600 (1952). *

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AN INVESTIGATION OF THE CONVERSIONS OF SECONDARY-TERTIARY
 α -GLYCOLS OF THE ACETYLENE SERIES UNDER THE
 ACTION OF MERCURY SALTS

III. 2-METHYL-1,4-DIPHENYLBUTYNE-3-DIOL-1,2

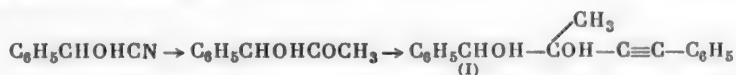
A. Fabritsy and E. D. Venus-Danilova

Previously one of us and V. M. Al'bitskaia [1, 2] established that, when treated with an alcohol solution of mercuric chloride, secondary-tertiary acetylene α -glycols (diphenyl-phenylacetyleneylethylene glycol and dimethyl-phenylacetyleneylethylene glycol) gave good yields of the corresponding furans (2,3,5-triphenyl- and 2,3-dimethyl-5-phenylfurans).

The same results were obtained by L. A. Pavlova [3] on treating a primary-secondary acetylene α -glycol (phenyl-phenylacetyleneylethylene glycol) with mercuric chloride and also with an alcohol solution of sulfuric acid. In both cases 3,5-diphenylfuran was isolated, but in the reaction with sulfuric acid, simultaneously with the substituted furan, the partial ethyl ether of the original glycol — 2-ethoxy-2,4-diphenylbutyn-3-ol-1 — was obtained.

In the present work we present the results of reacting another secondary-tertiary α -glycol of the acetylene series — 2-methyl-1,4-diphenylbutyne-3-diol-1,2 (I) — with mercuric chloride and sulfate in alcohol. In contrast to those examined previously, the molecule of this glycol contains a different type of substituent (aryl and alkyl) at the carbon atoms bearing hydroxyls.

The glycol was synthesized by the method of Iotsich from phenylacetylcarbinol and phenylacetylenyl-magnesium bromide. The phenylacetylcarbinol was prepared by treating mandelonitrile with methylmagnesium bromide according to literature data [4].



Considering the investigations of T. I. Temnikov [5] on the interconversions of methylbenzoyl- and phenylacetylcarbinols under the action of methylmagnesium bromide and phenylmagnesium bromide, we might expect that the synthesis of 2-methyl-1,4-diphenylbutyne-3-diol-1,2 would also give some of the isomeric 3,5-diphenylpentyne-4-diol-2,3 if the starting phenylacetylcarbinol were isomerized under the action of the phenylacetylenylmagnesium bromide. However, we isolated a single, normal reaction product, and the homogeneity of the glycol synthesized was confirmed by the products of its oxidation with lead tetraacetate — benzaldehyde and methyl phenylacetylenyl ketone — and the preparation from it of 3-methyl-2,5-diphenylfuran, which is described in the literature [6, 7], and not the isomeric 2-methyl-3,5-diphenylfuran.

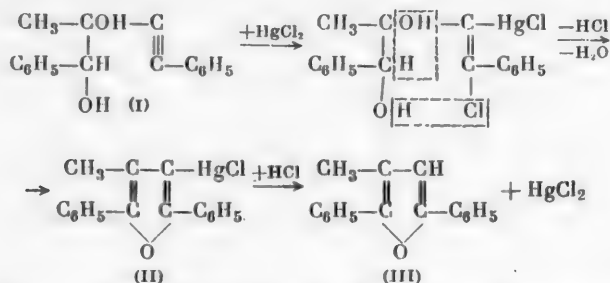
When treated with an alcoholic solution of mercuric chloride, the 2-methyl-1,4-diphenylbutyne-3-diol-1,2 very rapidly formed a voluminous, white, silky precipitate, which gradually dissolved on heating so that the final

reaction product was 3-methyl-2,5-diphenylfuran [6, 7] (III). The formation of a curdy precipitate and its gradual solution were also observed in the treatment of a primary-tertiary acetylene α -glycol with an alcohol solution of mercuric chloride [3].

It was found that the crystalline precipitate formed during the reaction of 2-methyl-1,4-diphenylbutyne-3-diol-1,2 with mercuric chloride contained chlorine and mercury and corresponded in properties and analysis data (Calculated %: Hg 42.88; Cl 7.59) to mercurated 3-methyl-2,5-diphenylfuran (II). The possible hypothesis that the organomercury compound was the product of the addition of mercuric chloride at the triple bond has to be rejected as in this case the substance should contain less mercury and more chlorine (Calculated %: Hg 38.38; Cl 13.58).

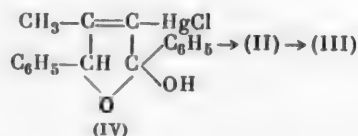
The organomercury compound obtained was quite stable in neutral solution, did not change when boiled with alcohol and water and was converted into the substituted furan only when hydrochloric acid was added and the mixture heated.

On the basis of the data obtained, it is reasonable to assume that the conversion of secondary-tertiary α -glycols of the acetylene series under the action of mercuric chloride into the substituted furans proceeds through mercurated furans by the following scheme:



We should note that the amount of hydrochloric acid determined in the solution after separation of the mercurated furan (II) corresponded exactly to the theoretical if the starting glycol and mercuric chloride were taken in equimolecular amounts (1:1). Changing the ratio of glycol to mercuric chloride so that the amount of mercuric chloride was decreased (1:0.5) had little effect on the yield of substituted furan (III), as was noted in previous investigations [1-3]. Evidently, the mercuric chloride obtained by thermal decomposition of the mercurated furan (II) may again react with glycol, if the latter is in excess of the mercuric chloride.

The proposed mechanism for the formation of substituted furans from secondary-tertiary acetylene α -glycols under the action of mercuric chloride explains the role of the mercuric chloride in this reaction. However, if we consider the formation of a mercurated ethylene γ -keto alcohol in the reaction of an unsymm. dimethyl-phenyl-phenylacetylenylethylene glycol with mercury salts [8, 9], we could suppose that substituted furans also are obtained from secondary-tertiary acetylene α -glycols by the method proposed previously [8], namely through the stage of allene rearrangement of the addition product of the mercury salt to the glycol with the formation of a mercurated ethylene γ -keto alcohol and cyclization of this into the mercurated hydroxydihydrofuran (IV). On losing water, the latter gives the mercurated furan (II), which is converted into substituted furan (III) by the action of hydrochloric acid.



However, the second scheme is less probable than the first.

When 2-methyl-1,4-diphenylbutyne-3-diol-1,2 was heated with mercuric sulfate in alcohol, 3-methyl-2,5-diphenylfuran was also isolated, but we have examined neither the intermediate product (mercurated furan) nor the mechanism of this reaction as yet. It is reasonable to assume that in this case, as with mercuric chloride, the first stage is the addition of mercuric sulfate at the acetylene bond of the glycol to form the unstable cyclic

organomercury compound. This compound is dehydrated and cyclized to form the β -mercuroorganic compound of furan, which loses mercuric sulfate and is converted into the substituted furan. A similar scheme was proposed by I. N. Nazarov and S. G. Matsoian [10] to explain the cyclohydration of acetylene γ -glycols into furanones in the presence of mercuric sulfate.

EXPERIMENTAL

1. Synthesis of 2-methyl-1,4-diphenylbutyne-3-diol-1,2 (I)

The starting phenylacetylcarbinol was prepared by treating mandelonitrile [4] (34.5% yield on benzaldehyde) with methylmagnesium bromide. The b.p. was 126-128° (16 mm).

For the synthesis of 2-methyl-1,4-diphenylbutyne-3-diol-1,2, we used 9.5 g of magnesium, 38 g of methyl bromide, 37 g of phenylacetylene and 22 g of phenylacetylcarbinol. To the phenylacetylenylmagnesium mide, prepared in the usual way, was added an ether solution of phenylacetylcarbinol over a period of 2 hours with stirring and cooling. When all the phenylacetylcarbinol had been added, the reaction mixture was heated for half an hour so that the ether boiled gently, then, after a day, decomposed with ammonium chloride solution and extracted with ether and the ether extract dried with sodium sulfate. After removal of the ether and phenylacetylene (in vacuum), a thick, sirupy product remained, which crystallized only after prolonged storage. Recrystallization from a mixture of petroleum ether and benzene (5:1) yielded 20 g (54.7%) of a substance with m.p. 82-83°. The substance was readily soluble in ether, benzene and alcohol, difficultly soluble in petroleum ether, decolorized an aqueous solution of potassium permanganate and bromine in chloroform and reacted vigorously with methylmagnesium bromide. When decomposed with potassium carbonate at 260°, the substance gave phenylacetylene, which was detected by the formation of a precipitate with an ammoniacal solution of silver oxide.

Found %: C 81.25, 81.18; H 6.53, 6.54; OH 13.79, M 243.5, $C_{17}H_{14}(OH)_2$. Calculated %: C 80.95; H 6.35; OH 13.49. M 252.

According to analysis data, the substance with m.p. 82-83° was a secondary-tertiary acetylene α -glycol.

Oxidation of the glycol with lead tetraacetate [11]. 5.4 g (20% excess) of lead tetraacetate was added in small portions with stirring to a solution of 2.5 g of the glycol in 25 ml of glacial acetic acid. When all the oxidant had been added, the reaction mixture was heated at 60-65° for 2 hours. After one day, the bulk of the acetic acid was neutralized with an aqueous solution of potassium carbonate and the oxidation product steam-distilled; three fractions of distillate (15-20 ml each) were collected. Each fractions was extracted with ether and the ether extracts were washed with water until neutral and dried with sodium sulfate. Removal of the ether from all the fractions gave small amounts of liquid products.

A 2,4-dinitrophenylhydrazone was prepared under the usual conditions [12] from the liquid of the 1st and 2nd fractions and a semicarbazone from the 3rd fraction.

The 2,4-dinitrophenylhydrazone melted at 186-186.5° (from glacial acetic acid).

Found %: C 58.99, 58.94; H 3.99, 4.00; N 17.12, 17.19. $C_{16}H_{12}O_4N_4$. Calculated %: C 59.26; H 3.70; N 17.28.

In melting point [13] and analysis data, the 2,4-dinitrophenylhydrazone corresponded to that of methyl phenylacetylenyl ketone (1-phenylbutyn-1-one-3).

The semicarbazone had m.p. 221-222° (from alcohol), which corresponded to the m.p. of benzaldehyde semicarbazone and did not depress the melting point of an authentic sample.

Found %: N 25.50, 25.78. $C_8H_5ON_3$. Calculated %: N 25.76.

In addition to the methyl phenylacetylenyl ketone and benzaldehyde, the oxidation products also yielded a very small amount of benzoic acid (mixed melting point) with m.p. 121° (after sublimation).

2. Action of Mercuric Chloride on 2-methyl-1,4-diphenylbutyne-3-diol-1,2

All the experiments were performed in a flask with a reflux condenser and a stirrer at the boiling point of the alcohol, in contrast to the experiments described previously [1, 2], in which the reaction was performed at 100° in sealed tubes.

3 g of glycol and 6.5 g of mercuric chloride (1 mole of glycol to 2 moles of mercuric chloride) were dissolved separately in a total of 45 ml of 95% ethyl alcohol. A minute after the solutions had been mixed, a white, crystalline silky precipitate began to form, the amount rapidly increased and after a short time, the whole mass solidified. When heated for 1 hour, the precipitate almost completely dissolved. The solution was cooled and filtered and the precipitate on the filter (m.p. 230-235°) was not examined more closely due to its small amount (~0.1 g). The filtrate was diluted with 200 ml of water and the oily substance liberated was extracted with benzene and dried with sodium sulfate. Removal of the benzene under reduced pressure yielded a solid substance with m.p. 58-59° (from methyl alcohol). The product was readily soluble in benzene and ether, less soluble in alcohol, decolorized a chloroform solution of bromine and an aqueous solution of potassium permanganate on heating and gave a weak blue fluorescence with concentrated sulfuric acid, which disappeared when the solution was diluted with water; the substance gradually became yellow on storing. According to analysis, it did not contain carbonyl or hydroxyl groups and was 3-methyl-2,5-diphenylfuran, which is described in the literature [6, 7]. We obtained 2.4 g (86.2%).

Found %: C 86.92, 86.82; H 5.98, 6.18. M 226.5. $C_{17}H_{14}O$. Calculated %: C 87.18; H 5.99. M 234.

We performed two further experiments under the same conditions with the same amount of glycol, but with different amounts of mercuric chloride - 1 mole and 0.5 mole of mercury salt to 1 mole of glycol. 3-Methyl-2,5-diphenylfuran with m.p. 58-59° was isolated in both cases in 82.6% yield.

In order to investigate the crystalline precipitate initially formed, a 4th experiment was performed with 3 g of glycol and 3.25 g of mercuric chloride (1:1). The reaction mixture was kept at room temperature for 3 days and then the fine, crystalline precipitate was filtered off, washed several times with alcohol and dried in a desiccator. The m.p. was 237-238° (from benzene).

The filtrate, diluted with water, (acid reaction) did not contain any organic material; it was found that all the mercuric chloride had reacted, since the filtrate contained only 0.077 g of mercury (as HgS), which corresponds to 0.1 g of mercuric chloride. 0.4342 g of chlorine was found; allowing for the chlorine present in the residual mercuric chloride, this represents 0.408 g of chlorine (or 0.418 g of HCl) liberated as hydrochloric acid in the reaction of the glycol with mercuric chloride. Theoretically, the solution should have contained 0.422 g of chlorine (0.434 g of HCl), which agrees well with the analysis data.

The crystalline substance isolated with m.p. 237-238° contained mercury and chlorine, did not contain hydroxyl groups, sluggishly decolorized a chloroform solution of bromine and an aqueous solution of potassium permanganate, was sparingly soluble in most organic solvents and was not changed on boiling with water.

Found %: Hg 42.45, 42.51; Cl 7.28, 7.39. $C_{17}H_{13}OClHg$. Calculated %: Hg 42.88; Cl 7.59.

The molecular weight was not determined due to the insignificant solubility of the substance in organic solvents.

Judging by the analysis data and the properties, the substance was 3-methyl-2,5-diphenyl-4-chloromercurifuran (II). We obtained 4.9 g (87.8%).

In a special experiment, an examination was made of the crystals precipitated immediately after the alcohol solutions of glycol and mercuric chloride were mixed (after 10-15 minutes). The precipitate was also 3-methyl-2,5-diphenyl-4-chloromercurifuran (II) (m.p. 237-238°).

When 1 g of 3-methyl-2,5-diphenyl-4-chloromercurifuran with alcohol was heated on a boiling water bath for 6 hours, the substance was recovered unchanged. Only when 0.5 ml of hydrochloric acid (d 1.16) was added to the reaction mixture, did the precipitate decompose rapidly. Dilution with water and extraction with benzene yielded 0.49 g (87.3%) of 3-methyl-2,5-diphenylfuran (III) with m.p. 58° from 1 g of mercurated furan (II).

3. Action of mercuric sulfate on 2-methyl-1,4-diphenylbutyne-3-diol-1,2

3 g of the acetylene glycol (m.p. 82-83°), 3.54 g of mercuric sulfate (1 mole:1 mole) and 50 ml of 80% ethyl alcohol were used. A large part of the mercuric sulfate did not dissolve during mixing and a yellowish precipitate was formed. After being heated for 3 hours on a boiling water bath, the mixture was poured with stirring into 300 ml of water. Removal of the benzene from the extracts yielded 1.74 g (62.5%) of 3-methyl-2,5-diphenylfuran with m.p. 57-58°.

SUMMARY

1. 2-Methyl-1,4-diphenylbutyne-3-diol-1,2, which is not described in the literature, was synthesized and it was shown that when treated with mercuric chloride and sulfate, this glycol formed 3-methyl-2,5-diphenylfuran.

2. When the glycol was treated with mercuric chloride, first there was formed an intermediate product from reaction of the glycol with mercuric chloride — 3-methyl-2,5-diphenyl-4-chloromercurifuran.

3. A mechanism for the conversion of 2-methyl-1,4-diphenylbutyne-3-diol-1,2 into 3-methyl-2,5-diphenylfuran was proposed.

LITERATURE CITED

- [1] E. D. Venus-Danilova and V. M. Al'bitskaia, J. Gen. Chem. 22, 816 (1952).*
- [2] E. D. Venus-Danilova and V. M. Al'bitskaia, J. Gen. Chem. 22, 1568 (1952).*
- [3] L. A. Pavlova, J. Gen. Chem. 25, 1521 (1955).*
- [4] A. Weissberger et al., Lieb. Ann. 478, 112 (1930).
- [5] T. I. Temnikova, J. Gen. Chem. 10, 468 (1940).
- [6] W. Lauer, M. Lauer and A. Spielmann, J. Am. Chem. Soc. 55, 4923 (1933).
- [7] R. E. Lutz and C. E. McGinn, J. Am. Chem. Soc. 64, 2585 (1942).
- [8] E. D. Venus-Danilova and A. Fabritsy, J. Gen. Chem. 26, 1609 (1956).*
- [9] E. D. Venus-Danilova and A. Fabritsy, J. Gen. Chem. 26, 1901 (1956).*
- [10] I. N. Nazarov and S. G. Matsoian, J. Gen. Chem. 27, 2951 (1957).*
- [11] New Methods in Preparative Organic Chemistry. For. Lit. Press, 150 [Russian translation] (1950).
- [12] V. Shriner and V. Fuson, Systematic Analysis of Organic Compounds. For. Lit. Press, 173 [Russian translation] (1950).
- [13] N. K. Kochetkov, J. Gen. Chem. 23, 760 (1953).*

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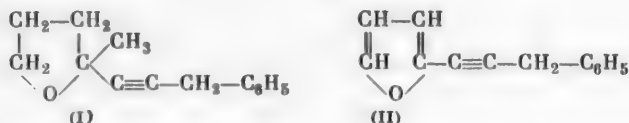
THE MECHANISM OF DEHYDRATION OF γ -GLYCOLS

VL. STUDY OF THE DEHYDRATION OF 3-METHYLHEXYNE-1-DIOL-3,6

T. A. Favorskaia and O. V. Sergievskaja

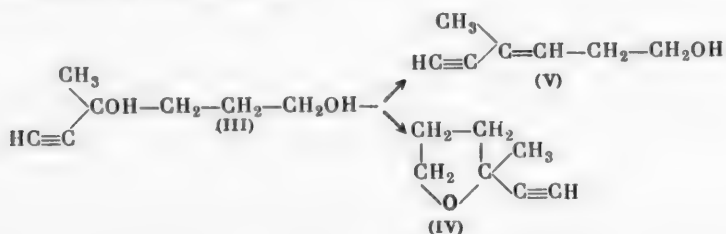
In studying the dehydration of γ -glycols, we showed [1-3] that the ethylene alcohols formed as a result of this reaction very readily isomerized into derivatives of tetrahydrofuran, with the exception of 2-phenylpenten-2-ol-5, which contains a system of conjugated bonds in its molecule and was not isomerized into 2,2-methylphenyltetrahydrofuran; the latter was formed from the glycol under considerably more drastic conditions by the elimination of water from the two hydroxyl groups.

With the intention of preparing 2,2-methylbenzylacetylenyltetrahydrofuran (I), an analog of the antibiotic, carlene oxide (II) [7], we synthesized the acetylene γ -glycol, 3-methylhexyne-1-diol-3,6 [4] (III) and studied its dehydration for the preparation of 2,2-methylacetylenyltetrahydrofuran (IV).



In most cases, the many experiments we performed on the dehydration of the glycol (III) gave insignificant yields of (IV) (10-47%) due to the formation of the enyne alcohol (V), which readily polymerized in an acid medium and gave a considerable amount of tar, as was shown previously [5].

The reaction proceeded in two directions:

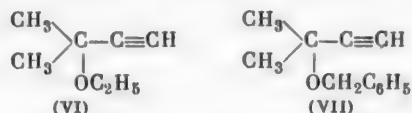


The alcohol (V), 3-methylhexen-3-yn-1-ol-6, was not isomerized into a tetrahydrofuran derivative, due to the presence of a stable system of a conjugated double and triple bond in it. We attempted to isomerize it under more drastic conditions by distillation in the presence of concentrated sulfuric acid; part of the alcohol distilled unchanged and the bulk of it was thus converted into a tarry polymer. The formation of 2,2-methylacetylenyltetrahydrofuran in this case, as in the case of 2,2-methylphenyltetrahydrofuran, may be explained by the elimination of water from the two hydroxyl groups of the glycol.

The structure of 2,2-methylacetylenyltetrahydrofuran was proved by hydrogenating it over platinum black to give 2,2-methylethyltetrahydrofuran, which we had prepared previously [6]. In addition, the structure (II) was confirmed by plotting the Raman and infrared spectra.

Carlene oxide was synthesized in 20% yield by Pfau et al. [7] by the action of benzyl chloride on furylacetylenylmagnesium bromide. We attempted to synthesize 2,2-methylbenzylacetylenyltetrahydrofuran by the action of benzyl bromide on the sodium or potassium derivative of 2,2-methylacetylenyltetrahydrofuran in liquid ammonia. As a result of the reaction, a considerable part of the starting material was recovered unchanged and the rest was converted into a nitrogen-containing substance with m.p. 98°, which we did not examine more closely. An attempt to isolate the sodium derivative of the product (IV) and react it with benzyl bromide in absolute ether was also unsuccessful. It was not possible to prepare the Na-derivative of 2,2-methylacetylenyltetrahydrofuran in boiling xylene, either. It was then decided to determine whether the sodium derivative formed in liquid ammonia was a derivative of 2,2-methylacetylenyltetrahydrofuran. When the reaction product was decomposed with water, part of the starting material was recovered and the other part was converted into a product, which, though it was unsaturated, did not give a precipitate with an ammonia solution of silver oxide and did not absorb in the infrared in the region of 2100-2140 cm^{-1} , characteristic of a triple bond; this product did not contain nitrogen, did not react with 2,4-dinitrophenylhydrazine solution, but reacted vigorously with methylmagnesium iodide. It was thus obvious that under the action of sodium, 2,2-methylacetylenyltetrahydrofuran underwent some deep conversion, which also explained the impossibility of preparing the required tetrahydrofuran derivative in this way.

The conversions of 2,2-methylacetylenyltetrahydrofuran described compelled us to determine how the reaction of sodium and halogen derivatives would proceed with alcohols of the acetylene series—whether this would give ethers, or whether substitution of the acetylene hydrogen by the corresponding radical would occur. With this aim, we studied the reaction of dimethylacetylenylcarbinol with ethyl bromide and benzyl bromide and sodium in liquid ammonia. In the first case we obtained the ethyl ether of dimethylacetylenylcarbinol (VI), which was much lower-boiling than the alcohol, gave a precipitate with an ammonia solution of silver oxide and contained the amount of ethoxyl group required by the formula indicated.



The reaction of dimethylacetylenylcarbinol with sodium and benzyl bromide gave a substance which had a neutral reaction, did not contain a hydroxyl group, did not give a reaction for an acetylene hydrogen and did not form a precipitate with mercuric chloride solution. The molecular refraction found corresponded with the refraction calculated for the benzyl ether of dimethylacetylenylcarbinol (VII). The presence of a triple bond in the ether obtained was confirmed by plotting the infrared and Raman spectra. The compound obtained was hydrogenated over Pt-black to give the benzyl ether of dimethylethylcarbinol, whose constants agreed well with the literature data.

The acetylene ether obtained was ozonized and gave the normal ozonolysis products, formic and benzoyloxysobutyric acids, but in addition, in one of the experiments we isolated methacrolein and benzaldehyde and in another, methacrolein and benzoic acid. The formation of these products may be explained by oxidative cleavage of the C—O bond.

In addition to the ether described above, the reaction of dimethylacetylenylcarbinol with sodium and benzyl bromide always gave a small amount of a lower fraction, which crystallized on standing. This substance contained 10% of nitrogen, had m.p. 96-98° and did not depress the melting point of the crystalline nitrogen-containing substance obtained previously. The structure of this product was not investigated.

An attempt was made to substitute the acetylene hydrogen in the benzyl ether of dimethylacetylenylcarbinol with sodium and then with ethyl by a reaction in liquid ammonia; however, this attempt was not successful and the ether was recovered unchanged.

EXPERIMENTAL

I. Dehydration of 3-methylhexyne-1-diol-3,6 (III) with sodium bisulfite. This reaction was originally undertaken in connection with the need of purifying the glycol from traces of acetopropyl alcohol, which is the starting material in its synthesis, but in the study of the reaction products, it was found that part of the glycol was dehydrated to form 2,2-methylacetylenyltetrahydrofuran (IV) and the enyne alcohol (V). The yield of the purified glycol was only 28.5%

35 g of the glycol was shaken with a freshly prepared, saturated solution of sodium bisulfite in a bottle with a ground stopper. The reaction mixture was left overnight, then the reaction products were extracted with ether and dried with Na_2SO_4 . Removal of the solvent and distillation of the residue yielded the following fractions: 1st b.p. 125°, 7.5 g; 2nd b.p. 45-60° (26 mm), 2g; 3rd 78-90° (15-19 mm), 8 g; 4th 105-125° (15 mm), 2 g; 5th 130° (15 mm), 10 g.

The 1st and 2nd fractions were combined and distilled on a column. We obtained 6.6 g of 2,2-methylacetylenyltetrahydrofuran.

B.p. 123-124°, n_D^{20} 1.4404, d_4^{20} 0.9117; M_{rD} 31.78. $\text{C}_7\text{H}_{10}\text{O}$ F. Calculated 31.90.
Found %: C 75.64; H 9.24. M 103. $\text{C}_7\text{H}_{10}\text{O}$. Calculated %: C 76.36; H 9.09, M 110.

Due to the extreme volatility of the substance, the elementary analysis was performed several times both by Korshun's method and by Pregl's, but completely satisfactory results could not be obtained.

Hydrogenation of 2,2-methylacetylenyltetrahydrofuran. 1.71 g of the substance was hydrogenated over Pt-black. 697 ml of hydrogen (95% of theoretical, calculated on a triple bond) was absorbed. After removal of the solvent, the substance was distilled over metallic sodium. We obtained 0.2 g of material with b.p. 118-121° and n_D^{20} 1.4220.

According to literature data, 2,2-methylethyltetrahydrofuran has b.p. 118-122° and n_D^{20} 1.4230 [6].

2,2-Methylacetylenyltetrahydrofuran reacted readily in the cold with an ammonia solution of silver oxide.

The structure of 2,2-methylacetyltetrahydrofuran was confirmed by plotting the Raman and infrared absorption spectra. The former was plotted on an ISP-51 apparatus with a slit of 0.06" and an exposure of 5 hours.

The following frequencies (cm^{-1}) were obtained: 618 (4), 740 (2), 852 (3), 922 (6), 1004 (3), 1100 (2), 1171 (3), 1234 (broad), 1446 (5), 1483 (3), 2051 (2), 2108 (10), 2870 (broad), 2934 (very broad), 2983 (very broad). The frequency of 2108 cm^{-1} corresponds to the triple bond and the frequency 922 (6) cm^{-1} to the vibration frequency of the tetrahydrofuran skeleton [8].

The infrared absorption spectrum was plotted on an IKS-11 apparatus with an NaCl prism, d 58 μ , from 860 to 1300 cm^{-1} and from 1300 to 2200 cm^{-1} and with an LiF prism, d 15 \pm 2 μ , from 2930-3600 cm^{-1} .

The frequency of 3285 cm^{-1} corresponds to the valence oscillation of $\equiv\text{CH}$; the frequency of 2120 cm^{-1} corresponds to the valence oscillation of $-\text{C}\equiv\text{CH}$; 1100 cm^{-1} to valence oscillations of the $\text{C}-\text{O}-\text{C}$ group in the tetrahydrofuran ring [9]; 905 cm^{-1} to the oscillation of the tetrahydrofuran ring [8].

A second distillation of the fraction with b.p. 78-90° (15-19 mm), obtained in the bisulfite treatment of 3-methylhexyne-1-diol-3,6 (III), yielded about 5 g (16%) of a substance which corresponded to the enyne alcohol (V) and became yellow on standing, even in sealed ampules.

B.p. 87-89° (19 mm), n_D^{20} 1.4833, d_4^{20} 0.9247, M_{rD} 33.99. $\text{C}_7\text{H}_{10}\text{O}$ F. Calculated 33.58. The constants agreed satisfactorily with literature data [5]; b.p. 72-74° (4 mm), n_D^{20} 1.4847, d_4^{20} 0.9174, M_{rD} 34.40.
Found %: OH 14.93. $\text{C}_7\text{H}_{10}\text{O}$. Calculated %: OH 15.44.

Attempts were made to isomerize the alcohol obtained into a tetrahydrofuran derivative.

1) When distilled with a drop of sulfuric acid at normal pressure, part of the alcohol was recovered (b.p. 150-155°, n_D^{20} 1.4840) and a considerable part of the alcohol polymerized.

2) When the enyne alcohol was treated with sodium bisulfite solution under the conditions used for dehydration of the glycol (III), about half of the alcohol was recovered (b.p. 155°, n_D^{20} 1.4821) and the rest formed a tar.

The 4th fraction, obtained in the bisulfite treatment of glycol (III), with b.p. 125-130° (15 mm), was the original glycol (n_D^{20} 1.4715); it formed a silver acetylide only on heating.

II. Dehydration of glycol (III) under the action of sulfuric acid. When the glycol was distilled with the vapor from aqueous 5 and 10% sulfuric acid, the sole product was 2,2-methylacetylenyltetrahydrofuran (IV) with b.p. 118-126°, n_D^{20} 1.4420, d_4^{20} 0.9120. The yield was 10%. The bulk of the substance polymerized.

When the vapor of the glycol was passed through a tube filled with pumice soaked in concentrated sulfuric acid at 100-125° (25 mm), a mixture of 2,2-methylacetylenyltetrahydrofuran and enyne alcohol was formed and these distilled-off with water. The reaction was accompanied by strong tar formation.

*As in original - Publisher's note.

The best yield of 2,2-methylacetylenyltetrahydrofuran was obtained by distilling the glycol from a Wurtz flask, over pieces of pumice soaked in sulfuric acid, heated on Wood's alloy at 130-140° (40-35 mm). 40 g of glycol yielded 30 g of a crude mixture of the cyclic product and enyne alcohol. Distillation yielded 15 g (47%) of 2,2-methylacetylenyltetrahydrofuran.

B.p. 124-125°, n_D^{20} 1.4397, d_4^{20} 0.9118, MR_D 31.78. $C_7H_{10}O$. Calculated 31.90.

The bulk of the enyne alcohol polymerized during distillation.

III. Unsuccessful attempts to prepare 2,2-methylacetylenyltetrahydrofuran. When the glycol (III) was distilled over $KHSO_4$ at 20 mm, the starting material distilled and part of the substance formed tar. When the glycol was distilled over oxalic acid (aqueous) at 115-120° (7 mm), the starting material was recovered.

9 g of the glycol was dissolved in 25 ml of wet ether, saturated with sulfur dioxide, the mixture again saturated with SO_2 and left overnight. After removal of the ether, the original glycol was distilled off and part of the substance formed tar.

When the glycol was distilled with the vapor from 0.4 and 1.6% sulfuric acid, the starting material was recovered.

Reaction of 2,2-methylacetylenyltetrahydrofuran with sodium and benzyl bromide in liquid ammonia. The reaction was performed in an open tube (6 cm diameter) with a capacity of 400-500 ml, fitted with a stirrer and placed in a Dewar vessel and cooled to -40 to -50° with a solution of carbon dioxide in ether. Into the tube was poured liquid ammonia (2/3 of the tube), followed by 15 g of 2,2-methylacetylenyltetrahydrofuran, and then 3 g of sodium was added in small pieces with stirring. The solution did not turn blue; the sodium disappeared rapidly and a portion of sodio derivative precipitated. After 30-40 minutes, 11 g of benzyl bromide, representing slightly less than the theoretical amount (12.4 g), was added. Stirring was continued until the precipitate of NaBr settled to the bottom. The mixture was left overnight, when the ammonia evaporated and next morning the reaction products were extracted with ether. The ether was removed and the residue vacuum-distilled. This gave the following fractions: 1st 33-38° (5-6 mm) in the receiver and 10 g of the starting material in a trap; 2nd 71-72° (4 mm), 4 g, n_D^{20} 1.5175, d_4^{20} 0.9537; 3rd 79° (4 mm), 2 g, n_D^{20} 1.5018.

The 2nd and 3rd fractions contained nitrogen, rapidly decolorized a solution of potassium permanganate and gradually crystallized as white plates with m.p. 98°.

The sodium derivative of 2,2-methylacetylenyltetrahydrofuran could not be obtained in xylene, even when the reaction mixture was boiled.

The sodium derivative of 2,2-methylacetylenyltetrahydrofuran was prepared in liquid ammonia as described above from 2.5 g of sodium and 12 g of 2,2-methylacetylenyltetrahydrofuran; after evaporation of the ammonia, the residual sodium derivative was boiled in anhydrous ether with 17 g of benzyl bromide for 4 hours. The following day, distillation of the reaction products gave an almost quantitative recovery of the starting materials.

Reaction of dimethylacetylenylcarbinol with sodium and ethyl bromide in liquid ammonia. 13 g of sodium was gradually added to 14 g of dimethylacetylenylcarbinol under the conditions described above for 2,2-methylacetylenyltetrahydrofuran. One hour after the beginning of the reaction, 19 g of ethyl bromide was added to the reaction mixture in small portions, avoiding vigorous boiling of the ammonia, and then stirring was continued for a further 1 hour. The following day, the reaction products were extracted with ether. After removal of the ether, the residue boiled at 89-91°. The yield was 7 g (37.5%). The substance gave a white precipitate with an ammonia solution of silver oxide and reacted with methylmagnesium iodide. Distillation on a column yielded 4 g of a substance which corresponded to the ethyl ether of dimethylacetylenylcarbinol (III).

B.p. 90-91°, n_D^{20} 1.4072, d_4^{20} 0.8035, MR_D 34.33. $C_7H_{12}O$. Calculated 34.17.

Literature data [10]: b.p. 93°; n_D^{20} 1.4042, d_4^{20} 0.8125.

Found% ethoxyl 40.50; number of active H atoms 0.56. $C_7H_{12}O$. Calculated % ethoxyl 40.17; number of active H atoms 1.

Apparently the acetylenic hydrogen does not react with methylmagnesium iodide completely; dimethylacetylenylcarbinol and other acetylene alcohols react with only one molecule of methylmagnesium iodide due to the hydrogen of the hydroxyl group.

Reaction of dimethylacetylenylcarbinol with sodium and benzyl bromide in liquid ammonia. The reaction was performed under the conditions described above. 4.4 g of sodium was added to 16 g of dimethylacetylenylcarbinol. 30 g of benzyl bromide was added to the sodium derivative formed. After evaporation of the ammonia, the reaction products were extracted with ether, the ether distilled off and the residue distilled on a column to give the following fractions: 1st 51-61° (2 mm), 1.2 g, n_D^{20} 1.5306; 2 g 62-74° (2 mm), 1 g. (Both fractions contained traces of halogen and crystallized on the walls of the flask).

A 3rd fraction of 11 g (36% calculated on the bromide taken) corresponded to the benzyl ether of dimethylacetylenylcarbinol (VII) and had the following constants.

B.p. 81-82° (2 mm), n_D^{20} 1.4990, d_4^{20} 0.9463, MR_D 53.95. $C_{12}H_{14}OF_3$. Calculated 53.65.
Found % C 82.36; H 8.43; M 172. $C_{12}H_{14}O$. Calculated % C 82.75; H 8.07, M 174.

For the substance with b.p. 81-82° (2 mm), we plotted the Raman spectrum on an ISP-51 apparatus with a slit of 0.005 and an exposure of 8-10 hours. The following data are the averages of three plots:

2108(8); 1604(5); 1452(2); 1376(1); 1207(2); 1158(1); 1026(6); 1000(10); 942(4); 820(1); 617(2) cm^{-1} . The frequency of 2108 cm^{-1} is characteristic of a triple bond and the frequencies 1604, 1000, and 617 cm^{-1} correspond to the C_6H_5 group.

The infrared absorption spectra were plotted on an IKS-11 apparatus with an LiF prism, d 15 μ , and intense absorption at 3308 cm^{-1} was observed and this is characteristic of the valence oscillations of the $\equiv C-H$ group.

In other experiments on the reaction of dimethylacetylenylcarbinol with sodium and benzyl bromide, the yield of reaction product was $\sim 40\%$; the product had b.p. 74.5-75° (1 mm), n_D^{20} 1.4995, d_4^{20} 0.9424.

Hydrogenation of benzyl ether of dimethylacetylenylcarbinol. 14 g of the substance with b.p. 74.5-75° (1 mm) was hydrogenated over 1.5 g of platinum black, when it absorbed 101% of the amount of hydrogen calculated for a triple bond. After removal of the alcohol, the residue was distilled to give 9 g of a substance corresponding to the benzyl ether of dimethylethylcarbinol.

B.p. 118.5°, n_D^{20} 1.4853, d_4^{20} 0.9175 [11], MR_D 55.72. $C_{12}H_{18}OF_3$. Calculated 55.66.
Found % C 80.85; H 10.31. $C_{12}H_{18}O$. Calculated % C 80.99; H 10.11.

Ozonization of benzyl ether of dimethylacetylenylcarbinol. 3 g of substance absorbed 1.11 g of ozone, which represents 130% of theoretical. When the ozonide had been decomposed with water, part of the solution was used for a formic acid determination by Fincke's method [12] (72%). Formaldehyde was not detected by a dimedone test. The neutral ozonolysis products were steam-distilled from the rest of the solution into a solution of 2,4-dinitrophenylhydrazine. The 2,4-dinitrophenylhydrazone obtained was difficultly soluble in alcohol and slightly more so in ethyl acetate. After several recrystallizations from the latter, it was separated into two products. The difficultly soluble product had m.p. 235° and did not depress the melting point of authentic benzaldehyde 2,4-dinitrophenylhydrazone (m.p. 234°) [13]. The 2,4-dinitrophenylhydrazone, which was readily soluble in alcohol and ethyl acetate, had m.p. 122°, after three recrystallizations from alcohol.

Found % N 22.32. Calculated for methacrolein 2,4-dinitrophenylhydrazone $C_{16}H_{19}O_4N_4$ % N 22.40.

The neutral solution of ozonolysis products was acidified with dilute sulfuric acid and the formic acid distilled-off. The solution of nonvolatile acids was neutralized with sodium carbonate, evaporated down, again acidified with sulfuric acid and then extracted with ether. After removal of the ether, the residue was placed in a vacuum desiccator over K_2CO_3 to remove the excess formic acid. As a result, we obtained 0.9 g of benzyloxyisobutyric acid as a brownish oil.

Found: equiv. 181.5. $C_{11}H_{14}O_3$. Calculated: equiv. 194.

0.82 g of the acid was dissolved in ammonia and after removal of the excess ammonia, the solution was treated with silver nitrate solution.

Found % C 44.30; H 3.90; Ag 37.71. $C_{11}H_{13}O_3Ag$. Calculated % C 43.85; H 4.32; Ag 36.21.

SUMMARY

1. It was shown that the dehydration of 3-methylhexyne-1-diol-3,6 proceeds in two directions to form 2,2-methylacetylenyltetrahydrofuran and an enyne alcohol - 3-methylhexen-3-yn-1-ol-6, which is largely polymerized under the reaction conditions.

2. It was shown that the enyne alcohol is not isomerized into 2,2-methyl acetylenyltetrahydrofuran.
3. It was shown that treatment of 2,2-methylacetylenyltetrahydrofuran with sodium produced deep changes in the structure of the tetrahydrofuran derivative, which made it impossible to prepare 2,2-methylbenzylacetylenyltetrahydrofuran, starting from 2,2-methylacetylenyltetrahydrofuran.
4. It was established that treatment of dimethylacetylenylcarbinol with sodium and halogen derivatives — ethyl bromide and benzyl bromide — in liquid ammonia yielded the corresponding ethers of dimethylacetylenylcarbinol.

LITERATURE CITED

- [1] T. A. Favorskaia and O. V. Sergievskaja, J. Gen. Chem. 25, 1509 (1955).*
- [2] T. A. Favorskaia and N. P. Ryzhova, J. Gen. Chem. 26, 423 (1956).*
- [3] T. A. Favorskaia, O. V. Sergievskaja and N. P. Ryzhova, J. Gen. Chem. 27, 937 (1957).*
- [4] T. A. Favorskaia and O. V. Sergievskaja, J. Gen. Chem. 28, 87 (1958).*
- [5] T. A. Favorskaia and L. S. Bresler, J. Gen. Chem. 27, 1179 (1957).*
- [6] T. A. Favorskaia and N. V. Shcherbinskaia, J. Gen. Chem. 23, 1667 (1953).*
- [7] A. St. Pfau, J. Pictet, P. Plattner and B. Suss, Helv. Chim. Acta. 18, 935 (1935).
- [8] H. Tschamler and H. Voelter, Monatsh. 83, 302 (1952).
- [9] Barrow and Searles, J. Am. Chem. Soc. 75, 1175 (1953).
- [10] A. N. Pudovik, J. Gen. Chem. 21, 1402 (1951).*
- [11] V. I. Isagulians and S. A. Skoblinskaia, J. Appl. Chem. 9, 1112 (1936).
- [12] H. Fincke, Bioch. Z. 51, 253 (1913).
- [13] V. S. Johnson, R. D. Shennan and R. A. Reid, Organic Reagents for Organic Analysis [Russian translation]** (1957).

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HOMOLOGS OF MONOVINYLACETYLENE

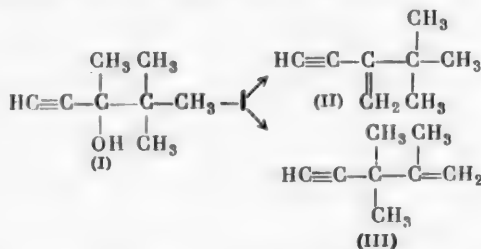
VIII. SPECTRAL CHARACTERISTICS OF AN ENYNE HYDROCARBON - 3',3'-METHO-3-ETHYLBUTEN-3-YNE-1 - AND ITS DERIVATIVES

Iu. P. Artsybasheva and I. A. Favorskaia

The present report is devoted to a spectral investigation of some unsaturated compounds with a tert-butyl group.

The inertness of 3,4,4-trimethylpentyn-1-ol-3 (I) in the substitution of the hydroxyl by halogen was noted previously [1] and the dehydration of this carbinol was studied. The structure of the hydrocarbon obtained in the dehydration was proved by oxidation with permanganate. Trimethylpyruvic acid was identified among the oxidation products as its *p*-nitrophenylhydrazone and on the basis of these data, the hydrocarbon was assigned the structure of 3',3'-metho-3-ethylbuten-3-yne-1 (II). However, since oxidation with permanganate is not as yet a quantitative method, we cannot exclude the possibility that the investigated hydrocarbon contained some of the isomeric hydrocarbon with unconjugated bonds - 3,4,4-trimethylpenten-4-yne-1 (III); this could also explain the anomalously low exaltation of the molecular refraction and the relative dispersion of the hydrocarbon.

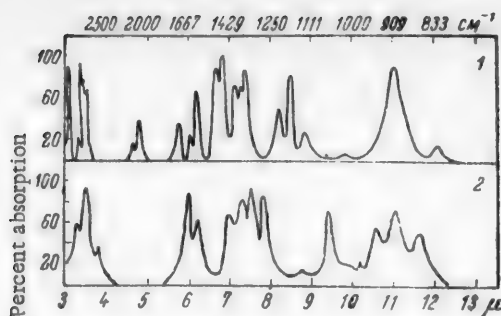
We were interested in the problem of the spectral proof of the structure of the products obtained by the dehydration of carbinol (I), from the point of view of a possible rearrangement with a change in the carbon skeleton, characteristic of saturated alcohols with a neopentyl grouping [2].



The carbinol (I) was dehydrated over anhydrous magnesium sulfate at 280-300°. The infrared absorption spectra of the products obtained were plotted. The spectrum (figure) showed bands indicating that the hydrocarbon obtained was the individual product (II) of a normal dehydration of the carbinol (I). The band at 1606 cm⁻¹ belonged to valence oscillations of the conjugated double bond [3] and the presence of a band at 2099 cm⁻¹ indicated the presence of a conjugated monosubstituted acetylene bond. A similar shift in the absorption bands from their normal position in the presence of conjugation in an enyne system, has been noted in the literature many times [4-8]. Bands indicating the presence of isolated double and triple bonds were not observed.

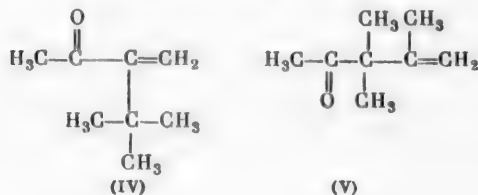
This makes the absence of exaltation of the molecular refraction and the low relative dispersion (ω_{FCD} 25.33) of the hydrocarbon [9] all the more interesting. This discrepancy may be explained by disruption of the coplanarity of the system due to steric hindrance caused by the tert-butyl radical. However, this postulate can only be confirmed by calculation and the construction of appropriate models, as will be done in the next report.

Interesting data were obtained in the spectral investigation of the hydration products of the hydrocarbon obtained. With a mixture of the hydrocarbons (II and III) present in the dehydration product of the carbinol (I), the



Infrared spectra. 1) 3',3'-methoxy-3-ethylbuten-3-yne-1 (II); 2) 3',3'-methoxy-3-ethylbuten-3-one-2 (IV).

hydration should give a mixture of conjugated - 3',3'-methoxy-3-ethylbuten-3-one-2 (IV) - and unconjugated - 3,4,4-trimethylpenten-4-one-2 ketones.



The infrared and ultraviolet absorption spectra of the hydration products were plotted. The infrared spectrum showed a band caused by the presence of a conjugated carbonyl (1689 cm^{-1}) and a double bond (1610 cm^{-1}) [3]. It is very difficult to indicate the

exact position of the absorption band of the double bond, due to the intense absorption of the carbonyl and the partial superposition of these bands. Intense absorption at 1361 and 1385 cm^{-1} [3] indicated the presence of a tert-butyl radical in the ketone. The absorption of the ketone in the ultraviolet region was characterized by the presence of two maxima at $\lambda_{\text{max}} 220 \text{ m}\mu$ ($\epsilon_{\text{max}} \sim 17000$) and $\lambda_{\text{max}} 304 \text{ m}\mu$ ($\epsilon \sim 21$).

According to literature data [10], α, β -unsaturated ketones have a strong ultraviolet band at $\lambda \sim 235 \text{ m}\mu$ ($\epsilon \sim 12000$) and a weak band at $\lambda 320 \text{ m}\mu$ ($\epsilon \sim 40$).

The presence of an intense band in the range $220\text{--}250 \text{ m}\mu$ in the spectrum of the carbonyl compound may be considered as proof of the conjugation of the ethylene and carbonyl groups; the long-wave band may be considered as a displaced carbonyl band. Consequently, on the basis of infrared and ultraviolet absorption spectral data, we may consider that the ketone corresponds to formula (IV) and is the hydration product of hydrocarbon (II).

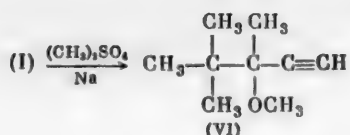
It is reported in the literature [11] that in going to ketone derivatives, there is an increase in the main absorption maximum and it is shifted towards longer wavelengths. Therefore, absorption spectra of derivatives are often used in the identification of carbonyl compounds.

It is known that semicarbazones of saturated ketones in alcohol have an intense band at $\lambda 228\text{--}230 \text{ m}\mu$ ($\epsilon \sim 10000\text{--}13000$), and the band typical of semicarbazones of α, β -unsaturated ketones appears in the range $260\text{--}273 \text{ m}\mu$ ($\epsilon \sim 20000$) [12]. A series of works has been devoted to the study of the absorption spectra of 2,4-dinitrophenylhydrazones [13].

We prepared derivatives of ketone (IV) and plotted their spectra. The spectrum of the semicarbazone had an absorption band at $233 \text{ m}\mu$ ($\epsilon 10000$), and the spectrum of the 2,4-dinitrophenylhydrazone of ketone (IV) in isooctane had a weak band at $408 \text{ m}\mu$ and an intense band at $348 \text{ m}\mu$ ($\epsilon 17000$). The data obtained indicate that the semicarbazone and the 2,4-dinitrophenylhydrazone of ketone (IV) have ultraviolet absorptions typical of derivatives of unconjugated ketones, while ketone (IV) itself absorbs like an α, β -unsaturated ketone.

Similar cases are also noted in the literature [14] for some cyclohexane derivatives. The semicarbazone of the α, β -unsaturated ketone, 2-n-butyl-1-acetylcyclohexene-1, has an absorption maximum at $226 \text{ m}\mu$ ($\epsilon 12000$), which agrees with the absorption maximum of the semicarbazone of the saturated ketone, 2-methyl-1-acetylcyclohexane ($\lambda 225 \text{ m}\mu$, $\epsilon 12300$). Evidently, in this case the absorption and intensity of the absorption band in the electron spectra depend on the character of the substituent, causing disruption of the coplanarity of the system. The absorption of nonplanar system is characterized by a fall in intensity and a hypsochromic effect.

It seemed interesting to us to methylate carbinol (I) to determine the effect of the tert-butyl radical on the possibility of substituting the hydrogen of the hydroxyl group and the substitution capacity of the free acetylenic hydrogen. The reaction gave the ether, 3,4,4-trimethyl-3-methoxypentyne-1 (VI) in 50% yield, calculated on the carbinol which reacted. Not even traces of an alcohol with a longer chain were found in the methylation products.



EXPERIMENTAL

Dehydration of 3,4,4-trimethylpentyn-1-ol-3 (I). The reaction was performed over anhydrous magnesium sulfate in a stream of nitrogen at 280-300°. The yield of hydrocarbon (II) was ~ 65%, calculated on the carbinol reacted. The hydrocarbon 3',3'-metho-3-ethylbuten-3-yne-1 was distilled twice on a column in a stream of nitrogen.

B.p. 47° (130 mm), n_D^{20} 1.43147, n_C^{20} 1.42841, n_F^{20} 1.43934, ω_{FCD} 25.33, d_4^{20} 0.7609, MR_D 36.74. $\text{C}_8\text{H}_{12}\text{F}$. Calculated 36.67. $\text{EMR}_D + 0.07$.

The hydrocarbon give a precipitate with an ammonia solution of silver oxide.

Spectrum of hydrocarbon plotted in the region 3-12 μ on an IKS-11 apparatus with NaCl and LiF prisms in a 50 μ layer. Found (in cm^{-1}): 830 w; 903 s; 1121 w; 1161 av; 1199 av; 1361 s; 1385 av; 1395 av; 1456 vs; 1478 s; 1606 av; 1681 w; 2099 av; 2154 w; 2863 s; 2904 s; 2958 vs; 3094 w; 3301 vs.

Hydration of hydrocarbon (II). Preparation of 3',3'-metho-3-ethylbuten-3-one-2 (IV). Into a three-necked flask, fitted with a stirrer, a reflux condenser and a thermometer, was placed 10 g of hydrocarbon (II), 2.4 g of mercuric oxide, 7 ml of concentrated sulfuric acid, 20 ml of a 50% solution of ferric sulfate and 170 ml of water. The reaction mixture was stirred vigorously and heated at 80° for 3 hours. The ketone was steam-distilled and extracted with ether. The ether extracts were dried with calcium chloride. The ketone was vacuum-distilled on a column.

B.p. 73-74° (96 mm), n_D^{20} 1.43465, n_C^{20} 1.43182, n_F^{20} 1.44171, ω_{FCD} 22.75; d_4^{20} 0.8513, MR_D 38.58. $\text{C}_8\text{H}_{14}\text{OF}$. Calculated 38.69.

Found % C 75.96; H 11.43. $\text{C}_8\text{H}_{14}\text{O}$. Calculated % C 76.13; H 11.18.

The infrared spectrum of the ketone was plotted on an IKS-11 apparatus with a layer thickness of 10 μ and NaCl and LiF prisms.

Found (in cm^{-1}): 855 av; 904 s; 942 av; 984 w; 1071 av; 1280 s; 1345 vs; 1365 s; 1385 av; 1442 av; 1610 av; 1689 s; 2868 vs; 3075 s.

The ultraviolet spectrum was plotted on an SF-4 apparatus. Found: λ_{max} 220 $\text{m}\mu$, ϵ_{max} 17000; λ'_{max} 304 $\text{m}\mu$, ϵ'_{max} 21 (in alcohol).

Semicarbazone of ketone (IV). The m.p. was 164-166° (alcohol).

Found % C 59.43; H 9.33; N 22.63. $\text{C}_9\text{H}_{17}\text{ON}_3$. Calculated % C 59.43; H 9.28; N 22.40.

Ultraviolet spectrum: λ_{max} 233 $\text{m}\mu$, ϵ_{max} 10900 (in alcohol).

2,4-Dinitrophenylhydrazone of ketone (IV). The m.p. was 109-111° (alcohol).

Found % C 54.64; H 6.18; N 18.19. $\text{C}_{14}\text{H}_{16}\text{O}_4\text{N}_4$. Calculated % C 54.89; H 5.92; N 18.28.

Ultraviolet spectrum: λ_{max} 348 $\text{m}\mu$, ϵ_{max} 16800 (in isooctane).

Methylation of carbinol (I). Into a wide tube, placed in a Dewar flask and cooled with carbon dioxide, was poured 250 ml of liquid ammonia. The reaction was performed at -34°. With stirring, 15 g of carbinol and 5.5 g of sodium in small pieces were introduced into the tube. When all the sodium had been added, the mixture was stirred for a further 20-30 minutes. Then dimethyl sulfate (15 g) was added over a period of 2 hours with vigorous stirring. When the ammonia had evaporated completely, water was added to the tube until the residue dissolved. The reaction products were extracted with ether. The ether extracts were washed with 2% acetic acid and water and dried over potassium carbonate. The product obtained was vacuum-distilled on a column. The 3,4,4-trimethyl-3-methoxypentyne-1 (VI) had the following constants:

B.p. 72-74° (95 mm), n_D^{20} 1.4294, d_4^{20} 0.8380. MR_D 43.62. $\text{C}_9\text{H}_{16}\text{OF}$. Calculated 43.40. $\text{EMR}_D + 0.22$. Found % C 77.30; H 12.02; OCH_3 20.98. $\text{C}_9\text{H}_{16}\text{O}$. Calculated % C 77.09; H 11.62; OCH_3 21.10.

SUMMARY

1. It was established that there was no rearrangement with a change in the carbon skeleton during the dehydration of 3,4,4-trimethylpentyn-1-ol-3.
2. Hydration of 3',3'-metho-3-ethylbuten-3-yne-1 yielded the ketone 3',3'-metho-3-ethylbuten-3-one-2, whose ultraviolet and infrared spectral characteristics corresponded to the characteristics of a conjugated α,β -unsaturated ketone.
3. It was shown that the semicarbazone and 2,4-dinitrophenylhydrazone of the α,β -unsaturated ketone, 3',3'-metho-3-ethylbuten-3-one-2 absorbed in the ultraviolet region like derivatives of saturated ketones.
4. 3,4,4-Trimethylpentyn-1-ol-3 was methylated. The ether, 3,4,4-trimethyl-3-methoxypentyne-1 was obtained.

LITERATURE CITED

- [1] I. A. Favorskaia, J. Gen. Chem. 18, 53 (1948).
- [2] F. C. Whitmore, J. Am. Chem. Soc. 54, 4011 (1932).
- [3] L. Bellamy, Infrared Spectra of Molecules [Russian translation] (1957).
- [4] J. L. Allan, Meakins and Whitting, J. Chem. Soc. 1875 (1955).
- [5] J. L. Allan and Whitting, J. Chem. Soc. 3314 (1953).
- [6] N. Sheppard, J. Chem. Phys. 17, 75 (1949).
- [7] R. Stamm, F. Halverson and J. Whalen, J. Chem. Phys. 17, 105 (1949).
- [8] A. A. Petrov, J. Gen. Chem. 27, 1167 (1957). *
- [9] B. V. Ioffe, Handbook of Refractometry for Chemists (1956). **
- [10] McMurry, J. Chem. Phys. 9, 241 (1941).
- [11] L. K. Evans and A. E. Gillam, J. Chem. Soc. 565 (1943).
- [12] A. Gillem and E. Shtern, Electronic Absorption Spectra of Organic Compounds [Russian translation] (1957).
- [13] I. N. Nazarov, L. A. Kazitsina and I. I. Zaretskaia, J. Gen. Chem. 27, 606 (1957). *
- [14] R. B. Turner and D. M. Viotle, J. Am. Chem. Soc. 73, 1403 (1951); E. A. Braude and E. R. Jones, J. Chem. Soc. 1890 (1949).

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THE CYANOETHYLATION OF ACETYLENE γ -GLYCOLS

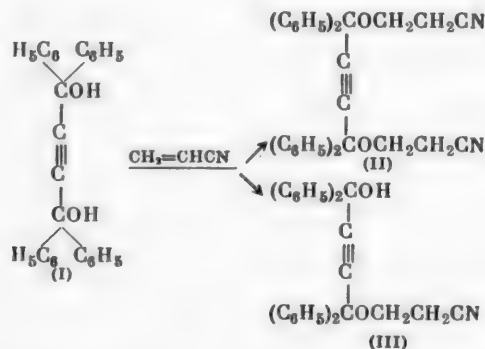
A. I. Zakharova and A. M. Efros

The addition of acrylonitrile to acetylene γ -glycols was first studied by Nazarov and Shvekhgeimer [1]. They cyanoethylated the simplest diprimary acetylene glycol — butynediol-1,4 — and the ditertiary acetylene glycol — tetramethylbutynediol — in the presence of a 40% aqueous solution of potassium hydroxide. The former smoothly added two molecules of acrylonitrile in dioxane solution to form the di(β -cyanoethyl) ether. Cyanoethylation of tetramethylbutynediol in this solvent required heating of the reaction mixture at 60-75° for 6 hours and this gave a mixture of the mono- and di-(β -cyanoethyl) ethers in approximately equal amounts.

Recently, one of us studied [2] the cyanoethylation in the benzimidazole series in the presence of triethylbenzylammonium hydroxide. It seemed interesting to test the possibility of using this catalyst in the cyanoethylation of unsaturated, hydroxy-containing compounds, in particular, acetylene γ -glycols. With this aim, we cyanoethylated two acetylene γ -glycols — tetramethyl- and tetraphenylbutynediols — in the presence of triethylbenzylammonium hydroxide. The cyanoethylation of tetramethylbutynediol in the presence of this catalyst proceeded very readily when a dioxane solution of the glycol was treated with a twofold excess of acrylonitrile and was accompanied by the evolution of a little heat and very slight tar formation. The reaction mixture was kept at room temperature for 24 hours and poured into water to deposit crystals of the di(β -cyanoethyl) ether of tetramethylbutynediol; after recrystallization from petroleum ether, the substance had m.p. 37-38°. The yield was 65%. • Under these conditions, the monocyanoethyl ether of the glycol is formed in a yield of not more than 8-10%.

Thus, it was found that triethylbenzylammonium hydroxide could be used successfully in the cyanoethylation of tetramethylbutynediol; the process proceeds under milder conditions than in the presence of 40% potassium hydroxide solution and the main reaction product — the di(β -cyanoethyl) ether of the glycol — precipitates immediately in the crystalline state and does not require long purification.

The cyanoethylation of tetraphenylbutynediol (I) in the presence of triethylbenzylammonium hydroxide also proceeded readily at room temperature as a result of the reaction of a dioxane solution of the glycol with a 2.5-fold excess of acrylonitrile. After standing for 48 hours, the reaction mixture deposited crystals which had m.p. 179-180° after recrystallization, and were the di-(β -cyanoethyl) ether of tetraphenylbutynediol (II). The yield was 52.6%. Working up the residual reaction mixture appropriately yielded the mono- β -cyanoethyl ether of the glycol (III) with m.p. 68-69°. The yield was 26.5%. Neither of the ethers are described in the literature.



• According to the data in [1], the di(β -cyanoethyl) ether of tetramethylbutynediol, after 5 distillations in vacuum, is a colorless, thick liquid, which crystallizes on standing; the m.p. is about 25°.

EXPERIMENTAL

Cyanoethylation of tetramethylbutynediol. Into a flask was placed 7 g of tetramethylbutynediol, 0.7 g of triethylbenzylammonium hydroxide and 10 ml of dioxane. 16.4 ml of acrylonitrile (twofold excess) was gradually added from a dropping funnel over a period of 30 minutes, when very slight tar formation was observed and the reaction mixture evolved heat. After 24 hours, the reaction mixture was poured into water and an oily layer was formed on the bottom of the flask, which crystallized when rubbed with a glass rod. The crystals were separated from the small amount of oily liquid and recrystallized, first from water and then from petroleum ether, when they melted at 37-38° and analyzed as the di(β -cyanoethyl) ether of tetramethylbutynediol. The yield was 8 g (65%).

Found %: C 67.98, 68.03; H 7.72, 8.03; N 11.52, 11.38. M 250. $C_{14}H_{20}O_2N_2$. Calculated %: C 67.74; H 8.07; N 11.29. M 248.

When distilled in vacuum, the uncrystallizable fraction, collected from several experiments, had b.p. 112-113° at 3 mm and was the mono- β -cyanoethyl ether of tetramethylbutynediol according to its constants [1].

Cyanoethylation of tetraphenylbutynediol. Into a two-necked flask, fitted with a reflux condenser and a dropping funnel, was placed 15 ml of dry dioxane, 15 g of tetraphenylbutynediol and 1 g of triethylbenzylammonium hydroxide. 10 g of acrylonitrile was gradually added at room temperature from the dropping funnel over a period of 15 minutes; slight tar formation was observed in the reaction mixture, but no noticeable heat evolution. After 48 hours, coarse crystals were deposited on the bottom of the flask and these were separated from the mother solution. After two recrystallizations from acetone and then from alcohol, the substance had m.p. 179-180°. A mixture with the original glycol (m.p. 199°) melted at 159-162°. The yield of the di(β -cyanoethyl) ether of tetraphenylbutynediol (II) was 10 g (52.6%).

Found %: C 82.54, 82.39; H 5.87, 5.74; N 5.69, 5.89. M 490. $C_{34}H_{28}O_2N_2$. Calculated %: C 82.23; H 5.67; N 5.62. M 496.

20 ml of water was added to the mother liquors left after separation of the crystals of the di-(β -cyanoethyl) ether of the glycol. A crystalline product precipitated and this was filtered off and recrystallized twice from petroleum ether. We obtained white, lustrous crystals of the mono- β -cyanoethyl ether of tetraphenylbutynediol (III) with m.p. 68-69°. The yield was 3 g (26.5%). The ether was readily soluble in alcohol.

Found %: C 83.99, 84.30; H 5.36, 5.43; N 3.11, 3.14. M 240. $C_{31}H_{26}O_2N$. Calculated %: C 83.92; H 5.63; N 3.15. M 248.

SUMMARY

1. The γ -acetylene glycols, tetramethyl- and tetraphenylbutynediol, were cyanoethylated with acrylonitrile in the presence of triethylbenzylammonium hydroxide.
2. It was shown that cyanoethylation in the presence of this catalyst proceeds under mild conditions without heating and that the reaction products are obtained in good yields.
3. The mono- and di-(β -cyanoethyl) ethers of tetraphenylbutynediol were prepared and characterized for the first time.

LITERATURE CITED

- [1] I. N. Nazarov and G. A. Shvekhgeimer, J. Gen. Chem. 24, 157 (1954).*
- [2] A. M. Efros, J. Gen. Chem. 28, 617 (1958).*

THE REACTION OF NITROSYL CHLORIDE WITH UNSATURATED HYDROCARBONS

IV. THE REACTION WITH BUTENE-1

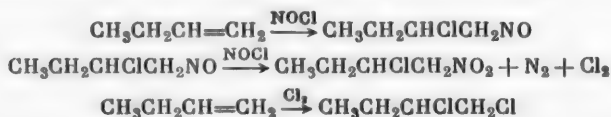
K. A. Ogloblin

In a previous communication [1] it was pointed out that the reaction of nitrosyl chloride with hydrocarbons containing an ethylene bond has mainly been investigated with tri- and completely substituted ethylene hydrocarbons, hydrocarbons of the cyclohexene series and in the terpene series [2], where it is often used to determine the degree of substitution of the carbon atoms at the double bond, but that it has hardly been investigated with mono- and disubstituted ethylenes.

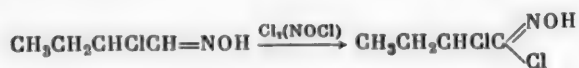
It was previously established that in the reaction of nitrosyl chloride with 2-methylbutene-3 [1], the main products were 4-nitro-3-chloro-2-methylbutane and 3,4-dichloro-2-methylbutanes, i.e., the primary reaction product, 4-nitroso-3-chloro-2-methylbutane, is oxidized by the nitrosyl chloride to the nitro compound and the chlorine liberated in the decomposition of the nitrosyl chloride gives the dichloride with the hydrocarbon. To determine how typical this reaction course was for other monosubstituted ethylene hydrocarbons, an investigation was made of the reaction of nitrosyl chloride with butene-1. The reaction was performed in ether solution, in sealed ampules at room temperature. As in the case of isopropyl ethylene, considerable pressure was generated in the ampules and this often burst the ampules. To decrease the possibility of bursting the ampule, the reaction was performed with less concentrated reagent solutions and only one third of the volume of the ampule was filled with the reaction mixture.

Butene-1 was more inert in the reaction with nitrosyl chloride than 2-methylbutene-3, which may be explained, on one hand, by the lower polarization of the double bond in butene-1 in comparison with 2-methylbutene-3 and also by the fact that the reaction with butene was performed with less-concentrated solutions.

As in the case of isopropyl ethylene, the main reaction products from butene-1 and nitrosyl chloride were the nitrochloro compound, 1-nitro-2-chlorobutane, and the dichloride, 1,2-dichlorobutane. The 1-nitroso-2-chlorobutane, formed in the first stage, was oxidized by the nitrosyl chloride to 1-nitro-2-chlorobutane and the chlorine, formed by decomposition of the nitrosyl chloride, gave the dichloride with the hydrocarbon.



The absence of the oxime of α -chlorobutyraldehyde from the reaction products indicated the very low rate of the rearrangement of the nitroso compound in comparison with the oxidation reaction. The presence of α -chlorobutyrohydroxyamyl chloride in the reaction products, indicated the formation of the chloro oxime, since the former was apparently produced by the action of chlorine or nitrosyl chloride on the oxime [3].



The structure of 1-nitro-2-chlorobutane was proved by converting it into α -chlorobutyric acid by heating it in sealed ampules at 140-145° [1].



Thus, as with 2-methylbutene-3, the reaction of nitrosyl chloride with butene-1 gives mainly the nitrochloro compound and the dichloride.

EXPERIMENTAL

Butene-1 was synthesized from allyl bromide and methylmagnesium iodide [4] and was used for the reaction without additional purification.

Nitrosyl chloride was prepared by reacting sodium nitrite with hydrochloric acid (d 1.19) [9]. To remove hydrogen chloride and oxides of nitrogen, the product was boiled for 30-40 minutes under reflux (minus 30-40°) and then distilled.

Reaction of nitrosyl chloride with butene-1. 98 g of nitrosyl chloride (-50°) was added with stirring to a solution of 51 g of butene-1 in 500 ml of anhydrous ether, cooled to -12° . The brown-red solution was poured into 19 ampules, cooled to -17° ; the ampules were sealed and placed in water at $+3^\circ$. The next day, the temperature of the bath was $+16^\circ$ and the ampules contained a brown-orange liquid without any red tinge. The next day the color of the reaction mixture was brownish green and on the third day, the homogeneous solution was slightly paler than on the day before. The ampules were cooled (-50°) and opened* by heating the ends with the flame of a torch, when high pressure was found to have been generated. The reaction mixture was washed three times with water, when the unreacted nitrosyl chloride was hydrolyzed to liberate brown vapors of nitrogen oxides, and the wash water was found to contain 12.1 g of hydrogen chloride.** The green ether solution was washed with 5% sodium carbonate solution (5×100 ml) and then twice with water. After being dried with anhydrous sodium sulfate, the ether solution had a light-green color. The volatile products were distilled in vacuum and caught in traps (-50°). The residue was vacuum-distilled. By subsequent distillations, the volatile products and residue were separated into fractions: 1st b.p. 41.5-42° at 40 mm, weight 13.6 g; 2nd b.p. 54-56° at 40 mm, 1.75 g; 3rd b.p. 56.5° at 4 mm, 18.0 g; 4th b.p. 77-78° at 4 mm, 2.3 g.

Investigation of fractions. 1st Fraction — a colorless, clear, mobile liquid.

d_4^{20} 1.1161, n_D^{20} 1.4445, M_{rD} 30.26; calc. 30.40.

Found % Cl 53.29, 53.65. $\text{C}_4\text{H}_9\text{Cl}_2$. Calculated % Cl 55.8.

The substance was 1,2-dichlorobutane (According to data in [5]: b.p. 123-125° at 758 mm, d_4^{20} 1.1187, n_D^{20} 1.440).

The 2nd fraction was a colorless mobile liquid with a pleasant smell, d_4^{20} 1.0520, n_D^{20} 1.4320. It was insoluble in water. It slowly decolorized a solution of potassium permanganate in acetone and did not reduce Fehling's solution. It gave qualitative reactions for nitrogen and chlorine (fusion with metallic sodium) and a nitrogen content of 2.6 and 2.3% (Dumas microdetermination). The substance was not identified.

The 3rd fraction was a colorless, clear liquid with a specific smell, insoluble in water and stable during storage.

d_4^{20} 1.2032, n_D^{20} 1.4510, M_{rD} 30.79;

Found % N 9.76, 10.06; Cl 25.98, 26.03. $\text{C}_4\text{H}_9\text{O}_2\text{NCl}$. Calculated % N 10.18; Cl 25.77.

The fraction was 1-nitro-2-chlorobutane (according to data in [6]: b.p. 78° at 13 mm, d_4^{20} 1.194, n_D^{20} 1.4480).

The 4th fraction was a clear, viscous liquid with d_4^{20} 1.3017, n_D^{20} 1.4864. It rapidly decomposed to form hydrogen chloride and colorless crystals (hydroxylamine hydrochloride). It was hydrolyzed by water, slowly in the cold and rapidly when heated. The aqueous solution had an acid reaction and gave a precipitate of silver chloride with silver nitrate solution and a reaction for hydroxamic acid with ferric chloride solution (red-violet color).

*One of the ampules was not opened for several more days, but no further noticeable changes in the color occurred.

**Before titration of the wash water, the nitrous acid was destroyed by the addition of thiourea.

The 4th fraction was α -chlorobutyrohydroxamyl chloride.

Conversion of 1-nitro-2-chlorobutane into α -chloro-n-butyric acid. To prove the structure of the nitro-chlorobutane, an investigation was made of the conversion of primary nitrohydrocarbons into carboxylic acids [7]. 5.3 g of 1-nitro-2-chlorobutane (b.p. 56.6° at 4 mm) and 10 ml of hydrochloric acid (d 1.19) were heated in a sealed ampule at 140-145° for 6 hours. The next day, colorless crystals appeared in the ampule in addition to the oily and the aqueous layer. The ampule was opened and contained a slight pressure. The contents of the ampule were diluted with water (the crystals dissolved completely) and the aqueous solution was treated with ether (6 x 20 ml); the oil passed into the ether solution, the latter was dried with sodium sulfate, the ether removed and the residue vacuum-distilled. Fractions of α -chloro-n-butyric acid were obtained: 1st, b.p. 68-72° at 4mm, 0.93 g, n_D^{20} 1.4453; 2nd, b.p. 72-74° at 4 mm, 2.2 g, d_4^{20} 1.1971, n_D^{20} 1.4407, M_{rD} 27.01; calc 27.07 (according to data in [8]: b.p. 101.25° at 15 mm, d_4^{20} 1.1796, n_D^{20} 1.4411).

Found: Neutralization equiv. 129.8. $C_4H_7O_2Cl$. Calculated: Neutralization equiv. 122.6.

The aqueous solution was evaporated to dryness. We obtained 1.72 g of hydroxylamine hydrochloride.

SUMMARY

1. The reaction of nitrosyl chloride with butene-1 in ether solution gave, as the main products, 1-nitro-2-chlorobutane and 1,2-dichlorobutane and a small amount of α -chlorobutyrohydroxamyl chloride.
2. The initial product — a chloronitroso compound — was oxidized to 1-nitro-2-chlorobutane and the chlorine, formed by decomposition of nitrosyl chloride, gave 1,2-dichlorobutane with butene.

LITERATURE CITED

- [1] K. A. Ogloblin, J. Gen. Chem. 27, 2541 (1957).
- [2] L. Beckham, W. Fessler and M. Kise, Chem. Revs. 48, 319 (1951).
- [3] H. Jale, Chem. Revs. 33, 209 (1943).
- [4] H. Lucas and R. Dillon, J. Am. Chem. Soc. 50, 1460 (1928).
- [5] D. Tishchenko and A. Churbakov, J. Gen. Chem. 7, 893 (1937).
- [6] J. Ville and G. Dupont, Bull. Soc. Chim. 804 (1956).
- [7] V. Meyer and J. Locher, Lieb. Ann. 180, 163 (1876).
- [8] E. Huntress, Organic chlorine compounds, N.Y. — London, 1260 (1948).
- [9] Inorganic Syntheses, N.Y. 4, 48 (1953).

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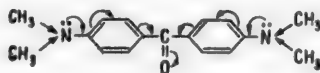
INVESTIGATION IN THE FIELD OF COMPOUNDS CONTAINING A THREE-MEMBERED OXIDE RING

XXIV. SYNTHESIS OF β,β' -DISUBSTITUTED NITRILES OF GLYCIDIC ACIDS

B. F. Martynov and A. V. Shchelkunov

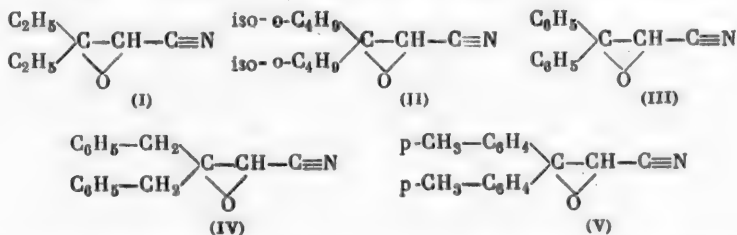
In a previous report [1], we described the reaction of monochloroacetonitrile with some ketones, which gave β,β' -disubstituted nitrile of glycidic acids, not described in the literature. To investigate the possibilities of synthesizing this class of compound, we reacted monochloroacetonitrile with a further series of ketones of aliphatic, aliphatic-aromatic and aromatic character, namely, diethyl, diisobutyl, dibenzyl, diphenyl, di-*p*-tolyl and di-*p*-dimethylaminophenyl ketones.

Of all the ketones listed here which underwent the condensation reaction, diisobutyl ketones gave the worst yield of final product. This is evidently explained by steric hindrance caused by the presence of the two isopropyl groups, which impede the approach of reagents to the carbonyl group. We should note that the reaction of this ketone (under the normal conditions) with ethyl monochloroacetate did not lead to the formation of a glycidic ester. As regards the other ketones, the highest yields of nitriles of glycidic acids were given by the aromatic ketones, diphenyl (81%) and di-*p*-tolyl ketones (80%). Michler's ketone did not condense with monochloroacetonitrile, despite many attempts to perform the reaction with freshly vacuum-distilled ketone. This can hardly be explained by steric hindrance, since the dimethylamino group is in a position para to the carbonyl. A more likely explanation may be found in peculiarities in the electronic structure of this ketone. It is known that the dimethylamino group possesses a very strongly expressed + I-effect, which may be readily transmitted through the benzene ring in a ketone with this structure and decrease the electrophilic properties of the carbonyl carbon atom.



Since there are two such groups here, their total effect may be so strong that the carbonyl group is practically incapable of adding nucleophilic reagents.

As a result of our work, we obtained the following five nitriles of glycidic acid.



Of these, the nitrile of diphenylglycidic acid is known [2], but the rest are not described in the literature.

An examination of the properties of the nitriles listed showed the great stability of the nitriles containing aromatic substituents. The other nitriles darkened in time and formed a brown precipitate. The more stable

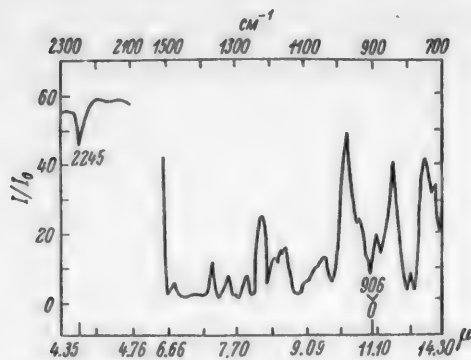


Fig. 1. Transmission spectrum of the nitrile of β,β' -dimethylglycidic acid (plotted with a thin layer with α 0.004 cm).

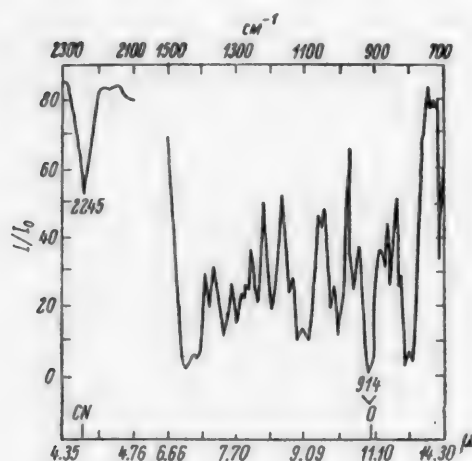


Fig. 2. Transmission spectra of the nitrile of β -pentamethyleneglycidic acid (plotted with a thin layer with α 0.006 cm).

nitriles could be vacuum-distilled. The nitriles of glycidic acids containing aliphatic radicals were almost impossible to obtain in a pure form — they always contained halogen. The traces of halogen may be explained by side reactions forming the α -chloronitrile of the corresponding unsaturated acid [3].

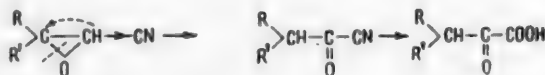
We plotted the Raman spectra of β,β' -dimethylglycidonitrile and confirmed this postulate: a weak band at the characteristic absorption frequency of a double bond (1662 cm^{-1}) was observed. In addition to the weak double bond line, the spectrum showed a very intense nitrile line (2245 cm^{-1}); guided by previous work [4], we assigned the line at 909 cm^{-1} to the oxide ring of β,β' -dimethylglycidonitrile. Together with this, a Beilstein test showed the presence of chlorine in a series of simple glycidonitriles. Carbon analyses, carried out after careful, repeated distillations of the β,β' -dimethyl- and β,β' -diethylglycidonitriles, gave low carbon percents and indicated the approximate content of the corresponding chlorocyclohexene. Similar mixtures contained about 97% of glycidonitrile.

Having a spectrum of the mixture, it seemed interesting to obtain a Raman spectrum of a pure glycidonitrile. The most convenient material for this purpose was β -pentamethyleneglycidonitrile [1]. Its spectrum showed a very intense nitrile group line (2245 cm^{-1}), the frequency of the cyclohexane ring (708 cm^{-1}) and the frequency of an oxide ring (914 cm^{-1}).

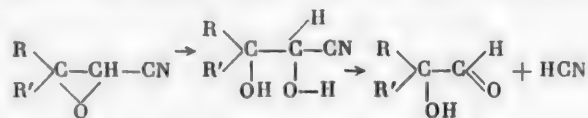
Besides the Raman spectra of the glycidonitriles, we also plotted their infrared spectra (Figs. 1 and 2); the latter confirmed the previous results. The infrared spectra were plotted on an IKS-11* with an NaCl prism.

To prove the structure of the glycidonitriles obtained, β -pentamethyleneglycidonitrile was hydrolyzed with acid. One would expect the following three directions for the hydrolysis of these compounds in the presence of concentrated sulfuric acid.

A. An initial isomerization of the starting glycidonitrile into the nitrile of an α -ketoxyacid; on hydrolysis the latter would give a disubstituted pyruvic acid.

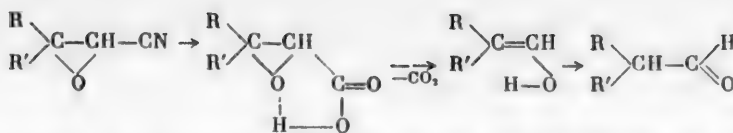


B. Opening of the oxide ring to form the nitrile of an α,β -dihydroxycarboxylic acid, which then may be cleaved to an α -hydroxyaldehyde and hydrogen cyanide under the conditions of the acid hydrolysis [5].



C. Saponification of the nitrile group of the glycidonitrile with subsequent formation of a glycidic acid, which is decarboxylated and the oxide ring opened to give the corresponding aldehyde.

* IKS-11 spectrometer — Publisher's note.



These conversions of glycidic acids in an acidic medium into the corresponding aldehydes have been described and are widely used nowadays as a method of preparing the latter [6]. The investigation performed showed that the acid hydrolysis proceeded mainly by mode C.

EXPERIMENTAL

The nitrile of β,β' -diethylglycidic acid (I). Into a three-necked, round-bottomed flask with a mercury seal and a stirrer was placed 10 ml of chloroacetonitrile and 13 ml of diethyl ketone (in this and subsequent syntheses, the starting materials were distilled immediately before the reaction; all the syntheses were performed in one day). Then approximately 100 ml of absolute ether was added and the flask with the reaction mixture cooled in ice and salt. When the temperature of the reaction mixture reached -10° , 13 g of dry sodium ethylate was added to it in small portions. The reaction proceeded with considerable heat evolution. The process was regulated so that the temperature of the reaction mixture did not exceed 0° . When all the sodium ethylate had been added, the contents of the flask were stirred for 30 minutes at -10° and for 1 hour at room temperature. As a result of the reaction, a precipitate of sodium chloride was formed. After being stirred, the reaction mixture was treated with water and the ether layer separated and dried with baked MgSO_4 . After removal of the ether, the residue was vacuum-distilled. The nitrile appeared as a colorless, mobile liquid with a weak smell. We obtained 10.6 g (53%).

B.p. $34-35^\circ$ (1 mm), $41-42^\circ$ (2 mm), d_4^{20} 0.937, n_D^{20} 1.4352, MR_D 34.82; calc. 34.50.
Found % N 11.33. $\text{C}_7\text{H}_{11}\text{ON}$. Calculated % N 11.20.

The nitrile of β,β' -diisobutyglycidic acid (II). 7.2 g of chloroacetonitrile, 18.6 g of isovalerone and 6.8 g of dry sodium ethylate were used. The reaction was performed in absolute ether. The nitrile was a colorless liquid with a weak smell. We obtained 6.4 g (35%).

B.p. $28-29^\circ$ (2 mm), d_4^{20} 0.8475, n_D^{20} 1.4170, MR_D 53.89; calc. 52.97.
Found % N 7.78. $\text{C}_{11}\text{H}_{19}\text{ON}$. Calculated % N 7.73.

The nitrile of β,β' -diphenylglycidic acid (III). 10 ml of chloroacetonitrile, 20 g of benzophenone and 6.5 g of dry sodium ethylate were used. The reaction was performed in absolute ether. Vacuum distillation of the reaction mixture yielded a fraction, which crystallized after some time. We obtained 19.7 g (81%). After two recrystallizations from ethyl alcohol, the substance appeared as colorless crystals with m.p. 72° .

Found % C 81.32; H 5.08; N 6.51; O 7.58. $\text{C}_{15}\text{H}_{11}\text{ON}$. Calculated % C 81.45; H 4.98; N 6.34; O 7.24.

The nitrile of β,β' -dibenzylglycidic acid (IV). 5.0 ml of chloroacetonitrile, 16.0 g of freshly distilled dibenzyl ketone and 5.0 g of dry sodium ethylate were used. The reaction was performed in absolute ether. The nitrile appeared as a slightly yellowish, oily liquid. We obtained 11.8 g (65%).

B.p. 197° (10 mm), d_4^{20} 1.0966, n_D^{20} 1.5667, MR_D 74.00; calc. 73.47.
Found % N 5.58. $\text{C}_{17}\text{H}_{15}\text{ON}$. Calculated % N 5.62.

The nitrile of β,β' -di-p-tolylglycidic acid (V). 3.2 ml of chloroacetonitrile, 13.4 g of di-p-tolyl ketone and 3.0 g of dry sodium ethylate were used for the reaction. The reaction was performed in absolute ether. The reaction product was isolated by vacuum distillation. We obtained 12.6 g (80%). After recrystallization from ethyl alcohol, the substance had m.p. 108° .

Found % N 5.66. $\text{C}_{17}\text{H}_{15}\text{ON}$. Calculated % N 5.62.

Acid hydrolysis of the nitriles of β -pentamethylene- and β,β' -dimethylglycidic acids. 5 ml of the nitrile of β -pentamethyleneglycidic acid, 15 ml of water, 5 ml of ethyl alcohol and 0.5 ml of concentrated sulfuric acid were heated for 10 hours on a boiling water bath in a sealed ampule until a homogeneous mass was obtained. The hydrolyzate was neutralized with BaCO_3 and steam-distilled. As a result, we obtained hexahydrobenzaldehyde

with b.p. 161°, d_4^{20} 0.9390, n_D^{20} 1.4667. A 2,4-dinitrophenylhydrazone with m.p. 142° was prepared. A mixed melting point with the 2,4-dinitrophenylhydrazone of an authentic sample of hexahydrobenzaldehyde was not depressed. The aldehyde yield was determined quantitatively by oximation. The aldehyde yield equaled 63%. We should also add that we isolated $(NH_4)_2SO_4$, formed as a result of saponification of the nitrile group.

The nitrile of β,β' -dimethylglycidic acid was hydrolyzed similarly. In this case, less sulfuric acid was used; one drop of concentrated sulfuric acid was used for 5 ml of an aqueous alcohol solution of the nitrile. The percent of aldehyde formed was determined by oximation. The aldehyde yield equalled 65%.

Raman spectrum of β,β' -dimethylglycidonitrile, containing traces of the α -chloronitrile of 2-methylcrotonic acid. (The intensities of the lines were evaluated visually).

328 (2), 360 (1), 433 (1), 477 (1), 543 (1), 696 (2), 783 (2), 909 (2), 1032 (1), 1089 (2), 1243 (1), 1298 (1), 1393 (1), 2245 (10), 2935 (1), 2986 (1).

The spectra were plotted on a Zeiss spectrograph with a slit width of 0.008 mm and an exposure of 3 hours.

Raman spectrum of β -pentamethyleneglycidonitrile (the intensities of the lines were evaluated visually).

216 (2), 294 (3), 368 (1), 475 (3), 557 (2), 632 (1), 679 (3), 708 (2), 787 (3), 808 (0.5), 831 (3), 865 (2), 914 (3), 1031 (2), 1093 (2), 1117 (2), 1200 (2), 1218 (2), 1273 (1), 1338 (1), 2245 (10), 2458 (1), 2955 (3).

The spectra were plotted on an ISP-51 spectrograph with a slit width of 0.004 mm and an exposure of 11 hours.

The fall in the basic characteristic frequency of the vibration oscillation of the cyclohexane ring from 802 to 708 cm^{-1} is probably explained by the strong +I-effect of the nitrile group, which could lead to a displacement of the electron densities of the carbon atoms of the cyclohexane ring.

SUMMARY

1. A study was made of the reaction of monochloroacetonitrile under the conditions of the Darzan reaction with some aliphatic, aliphatic-aromatic and aromatic ketones. It was shown that this reaction was quite convenient for the preparation of β,β' -disubstituted nitriles of glycidic acids.

2. 5 glycidonitriles which are not described in the literature, were synthesized and characterized.

3. It was established that Michler's ketone does not react with monochloroacetonitrile to form the corresponding glycidonitrile, which may be explained by the strong electron donor properties of the dimethylamino group.

4. An investigation was made of the acid hydrolysis of β -pentamethyleneglycidonitrile; this gave the corresponding aldehyde, which indicates that the hydrolysis began with saponification of the nitrile group.

LITERATURE CITED

- [1] V. F. Martynov and A. V. Shcheikunov, J. Gen. Chem. 27, 1188 (1957). *
- [2] F. Blicke and J. Faust, J. Am. Chem. Soc. 76, 3156 (1954).
- [3] M. Ballester, Chem. rev. 55, 283 (1955).
- [4] V. F. Martynov and G. Ol'man, J. Gen. Chem. 27, 1881 (1957). *
- [5] G. Favrel and C. Prevost, Bull. Soc. Chim. [4], 49, 243 (1931).
- [6] N. N. Suvorov, Prog. Chem. 17, (4) 432 (1948); Organic reactions, Vol. 5, p. 323 (1951).

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TELOMERIZATION OF CHLOROPRENE IN THE REACTION WITH 1,3-DICHLOROBUTENE-2 UNDER THE ACTION OF FeCl_3 . IV.

A. L. Klebanskii, A. G. Safadian and A. G. Barkhudarian

Telomerization, initiated by free radicals or ions, has attracted the attention of many investigators during recent years [1] as a method of organic synthesis and also as a method of preparing low-molecular polymers, which are used as plasticizers, film-forming materials etc.

In previous investigations [2], we studied the telomerization of 1,3-dichlorobutene-2 with chloroprene, isoprene and divinyl under the action of FeCl_3 , with a large excess of dichloride; low molecular compounds were mainly formed. Determination of the fractional composition of the telomers, obtained with various diolefins, showed that fractions with the greatest degree of telomerization ($n = 19$ for the 1st fraction) were obtained with isoprene. Chloroprene formed lower-molecular compounds ($n = 6$ for the 1st fraction). Divinyl occupied an intermediate position. Thus, in telomerization reactions under the action of ionic catalysts, the activity of chloroprene is lower than that of other diolefins. This is in contrast to the relatively great reactivity of chloroprene (whose rate is 760 times greater than that of isoprene) in radical polymerization, for reactions in a homogeneous mass.

In order to establish the effect of the ratio of 1,3-dichlorobutene-2 (I) to chloroprene (II) on the molecular weight of the telomers formed in the presence of FeCl_3 , in this work, we studied the telomerization over a wide range of molar ratios of (I):(II) — from 2:1 to 1:500. This was not only of theoretical interest, but had a certain practical value. The chloroprene distillate and especially the undistilled crude material contain traces of dichloride and FeCl_3 . The latter is formed as a result of the reaction of impurities with readily ionizable chlorine (4-chlorobutadiene-1,2, 1,3-dichlorobutene-2 and some dimers), contained in the chloroprene, with the material of the apparatus. The presence of dichloride and FeCl_3 in the chloroprene may cause the formation of a certain amount of low-molecular polymers during the distillation or during long storage. Preliminary experiments also showed that these impurities cause a change in the molecular weight and the plasticity of chloroprene polymers during polymerization in a homogeneous mass. In emulsion polymerization, these impurities did not have any noticeable effect on the process and the properties of the polymers, due to hydrolysis of the FeCl_3 and losses in catalytic activity. The results of experiments at various ratios of dichloride to chloroprene are presented in Table 1 and in Figs. 1-4.

The molecular weight of polymers with molecular weight of 5000 and less was determined cryoscopically in benzene and compared with the value found viscosimetrically. By comparison of the data obtained by the two methods, the relation between the viscosity and the molecular weight was expressed in the form of the power function $M = a[\eta]^b$ or $\lg M = \lg a + b \lg [\eta]$. This gave the following values for the constants.

- a) At an FeCl_3 concentration of 0.5 mole % $\lg a = 3.8390$, $b = 1.03297$.
 $\lg M = 3.8390 + 1.03297 \lg [\eta]$
- b) At an FeCl_3 concentration of 1 mole % $\lg a = 3.8972$, $b = 1.0945$.
 $\lg M = 3.8972 + 1.0945 \lg [\eta]$.

As is shown, the corresponding values of the constants agree closely in the two cases. Using these formulas, we calculated the molecular weights of polymers, for which these values were more than 5000.

The characteristic viscosities of various polymer homologs are presented in Figs. 1 and 2.

TABLE 1

Dependence of Yield and Mean Molecular Weight of Polymer on the Ratio of the Starting Materials (Duration of experiments 48 hours, temperature 50°, FeCl₃ concentration 0.5 mole % in series I and 1 mole % in series II)

Experiment No.	Molar ratio of dichloride to chloroprene	Yield of polymer on total monomers (in %)	Percent chlorine in polymer		Percent saponifiable chlorine in polymer		Characteristic viscosity $\eta_{sp}/(c \rightarrow 0)$	Mean molecular weight*			Calculated empirical formula	Calculated mean molecular weight from empirical formula
			found	calculated	found	calculated		viscosimetrically	cryoscopic in benzene	by saponified		
Series I	1 2 : 1	1.96	44.98	45.43	8.72	9.11			412.0	407	C ₁₆ H ₂₁ Cl ₃	390.5
	2 2 : 1	3.62	44.75	44.46	7.72	7.41			473.5	460	C ₂₀ H ₂₆ Cl ₆	479.0
	3 1 : 2	4.33	44.22	44.46	7.51	7.41			489.5	459.8	C ₂₀ H ₂₆ Cl ₆	479.0
	4 1 : 5	6.23	43.10	42.29	5.21	5.41	0.108	715	693.0	682.0	C ₂₃ H ₃₆ Cl ₈	656
	5 1 : 50	7.45	42.0	42.62	3.98	4.26	0.135	837.5	840.3	882.3	C ₃₀ H ₁₆ Cl ₁₀	833
	6 1 : 100	8.21	41.75	42.00	3.07	3.23	0.167	1097.0	1085.0	1156.0	C ₁₃ H ₆₁ Cl ₁₃	1098.5
7 1 : 500	9.25	38.47	39.4	0.61	0.70	0.722	4920.0	5065.5	5038.0	C ₂₂₄ H ₂₈₁ Cl ₅₇	5043	
Series II	1 1 : 2	5.11	44.12	43.79	6.72	6.25			542.5	527.6	C ₂₄ H ₃₁ Cl ₇	567.5
	2 1 : 5	7.45	43.04	42.37	3.92	3.85	0.142	933.0	891.5	905	C ₄₀ H ₅₁ Cl ₁₁	921.5
	3 1 : 50	10.35	41.85	41.34	2.00	2.07	0.243	1684.0	1670.0	1775	C ₇₆ H ₉₆ Cl ₂₀	1718.0
	4 1 : 100	12.7	39.82	40.49	1.30	1.32	0.364	2620	2615.5	2719	C ₁₂₀ H ₁₅₁ Cl ₃₁	2690.5
	5 1 : 500	15.54			0.64	0.69	0.708	5420	5125	5550	C ₂₃₂ H ₂₉₁ Cl ₅₉	5167
	6 1 : 1000	16.83	Not determined				1.043	5275				

* Determined after the polymers had been purified by solution in benzene and precipitation with methyl alcohol twice and then dried in vacuum in nitrogen.

TABLE 2

Solution concentration (g in 100 ml of benzene)	Flow time (sec)	Relative viscosity (η_{rel})	Specific viscosity (η_{sp})	Reduced viscosity $\eta_{sp}/(c \rightarrow 0)$
0.8709	97.6	1.5724	0.5424	0.175
0.705	94.4	1.1143	0.1143	0.1621
0.556	91.8	1.0838	0.0838	0.1507
0.4484	89.3	1.0561	0.0661	0.1476

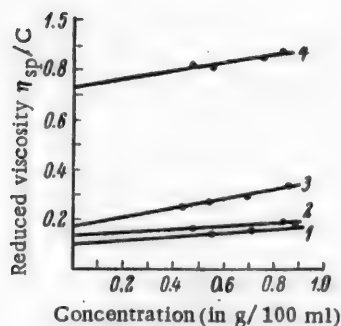


Fig. 1. Characteristic viscosities of solutions of polymer homologs, obtained with an FeCl_3 concentration of 0.5 mole %

Value of $\eta_{charact.}$: 1) 0.108 (expt. 4); 2) 0.135 (expt. 5); 3) 0.157 (expt. 6); 4) 0.722 (expt. 7).

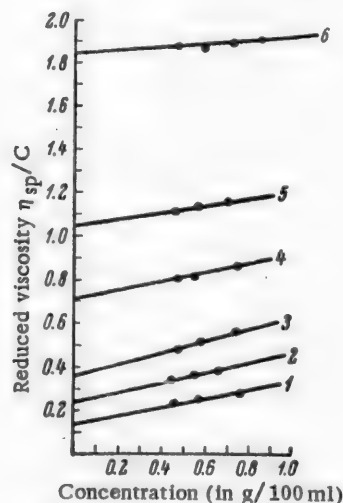


Fig. 2. Characteristic viscosities of solutions of polymer homologs, obtained with an FeCl_3 concentration of 1 mole %

Value of $\eta_{charact.}$: 1) 0.142 (expt. 2); 2) 0.243 (expt. 3); 3) 0.364 (expt. 4); 4) 0.78* (expt. 5); 5) 1.043 (expt. 6); 6) 1.85 (expt. 7).

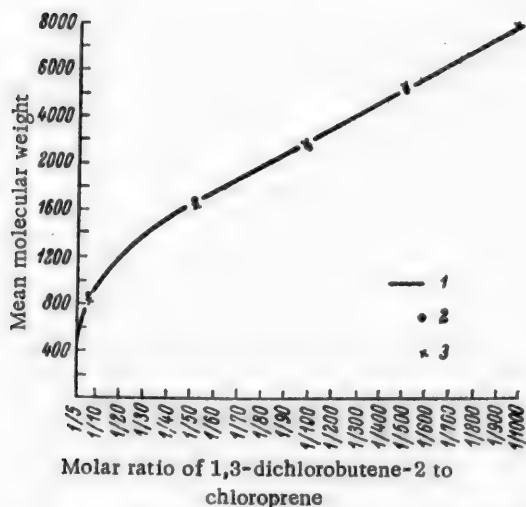


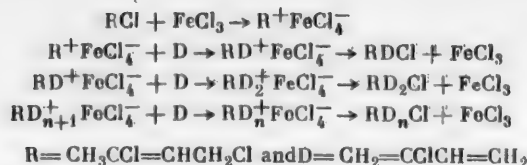
Fig. 3. Dependence of mean molecular weight of polymer on ratio of starting materials (the FeCl_3 concentration equaled 1 mole %).

1) Calculated theoretically; 2) determined by hydrolyzable chlorine; 3) determined cryoscopically in benzene.

* As in Russian. Probably is 0.708 — Publisher's note.

The data presented in Table 1 show that with a decrease in the ratio of 1,3-dichlorobutene-2 to chloroprene, both the yield and the mean molecular weight of the polymer formed increase. This is illustrated by the curves in Figs. 3 and 4.

The presence of hydrolyzable chlorine in all the fractions and the increase in the content of it as the molar ratio of 1,3-dichlorobutene-2 to chloroprene increases, and also the agreement between the molecular weights determined by the hydrolyzable chlorine and by other methods indicate the following scheme for the telomerization process:



The reaction studied can also be considered as a stepwise copolymerization of chloroprene and the dichloride, initiated by the cation-active catalyst FeCl_3 .

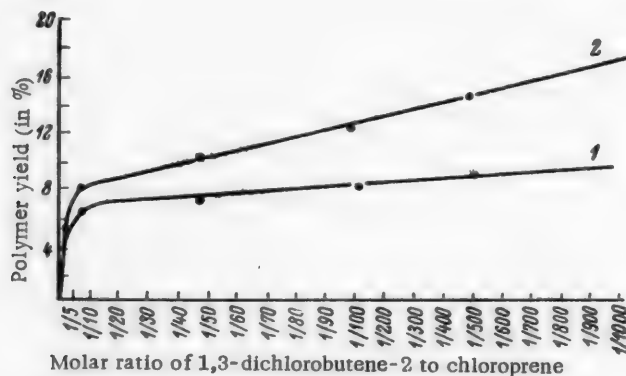


Fig. 4. Dependence of polymer yield on ratio of starting materials. FeCl_3 concentration (in mole %): 1) 0.5; 2) 1.

EXPERIMENTAL

133.2 g of chloroprene (1.505 mole), 1.9 g of 1,3-dichlorobutene-2 (0.015 mole) and 1.23 g of FeCl_3 (0.5 mole %) were heated in a sealed ampule in nitrogen, freed from oxygen, at 50° for 48 hours. The reaction product was washed with 10% HCl to remove the catalyst and then with water and dried with CaCl_2 . The unreacted chloroprene and dichloride were removed in vacuum. The residual polymers were purified by solution in a 10-fold excess of benzene and precipitation with methyl alcohol (1.5 volumes to one volume of benzene) twice. The precipitated polymers were dried to constant weight at a water-bath temperature of 100° at 100 mm in nitrogen and analyzed.

Found %: Cl 41.75, hydrolyzable Cl 3.07. $\text{C}_{48}\text{H}_{61}\text{Cl}_{13}$. Calculated %: Cl 42.0, hydrolyzable Cl 3.23.

Mean values of molecular weight found: cryoscopically (in benzene) 1085; chemically by hydrolyzable chlorine 1156; viscosimetrically 1097. $\text{C}_{48}\text{H}_{61}\text{Cl}_{13}$. Calculated M 1098.

The other experiments and analyses presented in Table 1 were performed similarly. As an example, we present data on the determination of the mean molecular weight from viscosity for polymers prepared with a dichloride: chloroprene ratio of 1:500. Solutions in benzene at four different concentrations were prepared and examined. The viscosity was determined in an Ostwald viscometer (Table 2).

The characteristic viscosity, $\eta_{\text{charact.}} = 0.777$ (Fig. 1) was determined graphically from the data obtained. The characteristic viscosities of all the polymers were determined similarly.

SUMMARY

1. A study was made of the telomerization of chloroprene in the presence of 1,3-dichlorobutene-2 under the action of FeCl_3 .

2. Investigation of the polymers obtained showed that 1,3-dichlorobutene-2 formed part of all the polymers in amounts which fell with a decrease in the molecular ratio of the dichloride to chloroprene; the mean molecular weights of the polymers increased correspondingly.

3. A satisfactory agreement was found between the molecular weights determined by the hydrolyzable chlorine, cryoscopically and viscosimetrically, and this confirms the scheme proposed for telomerization under the action of FeCl_3 .

LITERATURE CITED

[1] J. N. Breitenbach and A. Maschin, *Z. Phys. Ch.* 137A, 175 (1940); A. L. Klebanskii and R. S. Sorokina, Third Conference on High-Molecular Compounds, Acad. Sci. USSR Press, 10 (1948); * R. M. Joyll, W. E. Hanford and J. Harmon, *J. Am. Chem. Soc.* 70, 2529 (1948); T. Wagner-Jauregg, *Lieb. Ann.* 492, 52 (1932); T. Lennartz, *Ber.* 76, 831 (1943); E. L. Jenner and R. S. Schreiber, *J. Am. Chem. Soc.* 73, 4348 (1951).

[2] A. L. Klebanskii, A. G. Saadian and A. G. Barkhudarian, *J. Gen. Chem.* 28, 574, 881 (1958). **

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ON THE ORDER OF ADDITION OF LITHIUM TO BIPHENYL

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Schlenk and Bergmann [1] first showed that when an ethereal solution of biphenyl is shaken with lithium, the latter is almost quantitatively added to the biphenyl, a dilithium derivative being formed. On treatment of the latter with alcohol, dihydrobiphenyl is obtained; on treatment with carbon dioxide, dihydrobiphenylcarboxylic acid is formed. As in the catalytic hydrogenation of dihydrobiphenyl, cyclohexylbenzene was obtained, and when the dicarboxylic acid was boiled with acetic anhydride, the acid remained unchanged. Schlenk and Bergmann held that the addition of lithium to biphenyl occurs in the 1,4-position. Benkesser and co-workers [2] obtained cyclohexylcyclohexene-1 on reduction of biphenyl with lithium in a methylamine medium; on reduction of anisole [3] they obtained a mixture of 2,5- and 2,3-dihydroanisoles. The cited authors suggested that the addition of lithium to aromatic hydrocarbons occurs in the 1,4-position, and that the resulting quinoid system then isomerizes to a more stable conjugated system. Hückel and co-workers published two works on the reduction of biphenyl with sodium in liquid ammonia. In the first work [4] it was suggested that a conjugated double bond is initially formed, and one bond is then reduced.

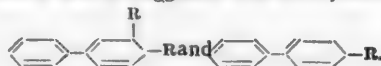


Seventeen years later, Hückel [5] revised his conclusions. Proceeding from ultraviolet spectra, and also on the basis of the results of hydrogenation and the absence of an adduct with maleic anhydride, Hückel holds that the addition of sodium to biphenyl occurs in the 1,4-position in both rings, and the product obtained has one of the following structures:



On reaction of dilithiumdihydrobiphenyl with alkyl halides [6] ($\text{C}_4\text{H}_9\text{Br}$, $\text{C}_6\text{H}_{13}\text{Br}$, $\text{sec-C}_8\text{H}_{17}\text{Br}$, $\text{C}_9\text{H}_{19}\text{Br}$ and $\text{C}_{10}\text{H}_{21}\text{Br}$), mono- and dialkylidihydrobiphenyls were obtained. Absorption bands were observed in the ultraviolet spectra of these hydrocarbons, which were similar in intensity and position to those in the spectra of biphenyl and phenylcyclohexene-1. On the basis of this we suggested that the hydrocarbons obtained may have the

following structures:



Continuing this work, we conducted the present investigation for the purpose of determining the positions of addition of lithium to biphenyl in greater detail. In connection with this, the ultraviolet and infrared absorption spectra of the following hydrocarbons, synthesized by us, were obtained.



The ultraviolet spectra were taken by the usual method in an ISP-22 spectrograph and SF-4 spectrophotometer, and the infrared spectra were obtained with an IKS-11 spectrometer equipped with LiF and NaCl prisms. The ultraviolet spectral data are shown in Fig. 1. On examining these data it may be seen that the spectra of

* The given structure is assigned on the basis of Schlenk's conclusions (which, as will be shown later, are erroneous).

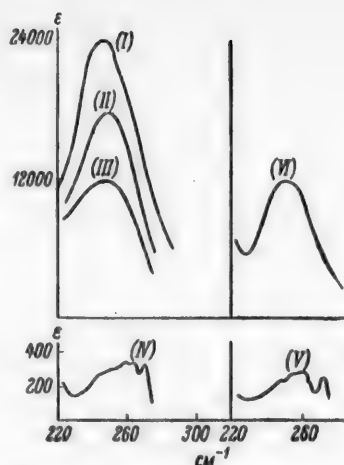


Fig. 1. Ultraviolet absorption spectra of the hydrogenation products of biphenyl. (Solutions in isooctane; ϵ is expressed in liters / mole \cdot cm).

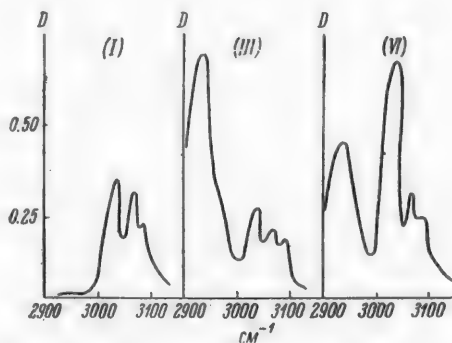
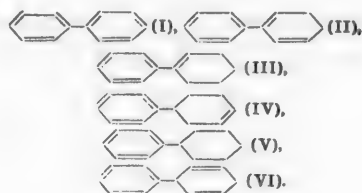
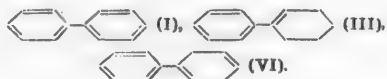


Fig. 2. Infrared absorption spectra in the 2900-3100 cm^{-1} region.



e.g., 1070, 1156, 1185, 1600 and 3030 cm^{-1} . 2) In the spectra of (I), (II), (III) and (VI) the $\text{C}=\text{C}$ wave number, 1600 cm^{-1} , is decreased to 1590 cm^{-1} , as is usually observed on conjugation of multiple bonds; in (IV) and (V) this wave number retains its value, 1600 cm^{-1} . The difference between the spectra of (I), (II), (III) and (VI) and those of (IV) and (V) is observed in other regions; in the infrared spectra of (I), (II), (III) and (VI), for instance,

(I), (II), (III) and (VI) sharply differ from those of (IV) and (V). The spectra of the first compound contain one broad and very intense band without appreciable fine structure. The intensity (ϵ) of this band at the maximum (250 $\text{m}\mu$) is 24,000 units for (I), 18,000 for (II), and about 12,000 for (III) and (VI). It follows from these data that a decrease in the number of conjugated bonds causes a corresponding decrease in the band intensity, and that the absorption-band intensity in (VI) is nearly the same as that in (III), i.e., in a compound in which one $\text{C}=\text{C}$ bond is conjugated with a benzene ring. The spectra of (IV) and (V) resemble each other and differ little from those of the well-known monosubstitution products of benzene. The absorption bands have a pronounced fine structure with values of ϵ equal to 200-400 units.

The data given do not support the quinoid structure of the second ring in (VI), since in the case of the quinoid structure we would observe (in view of the absence of conjugation of the $\text{C}=\text{C}$ bond with the benzene ring) a lower absorption-band intensity, approximating to that in the ultraviolet spectra of (IV) and (V). From the literature it is known [13] that the ultraviolet spectrum of an aromatic ring with a quinoid structure does not differ essentially from that of the cyclohexane ring; e.g., the ultraviolet spectra of tetralin and 1,4-dihydronaphthalene are similar. Therefore, taking into account the value of ϵ in the spectrum of (VI) (12,000),

we may imagine its structure to be


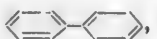
General speaking, we may assume also the existence of

a mixture of biphenyl and or (II) and or even and

In order to solve this problem we turned to the infrared absorption spectra. Spectra in the 2-15 μ region were obtained for (I-VI) with a NaCl prism. We paid particular attention to the 3-3.5 μ region, in which, as is generally known, the wave-numbers of the valence vibrations of the CH_2 and CH groups are located, and also to the 6-7 μ region, where wave-numbers characteristic of the valence vibrations of the $\text{C}=\text{C}$ group and the deformation vibrations of the CH_2 group are located. A LiF prism was used in the 3-4 μ region.

The following facts were ascertained on examination of the infrared spectra. 1) In all spectra there are observed wave numbers characteristic of aromatic hydrocarbons containing a monosubstituted benzene ring,

bands at 910, 1017 and 1045 cm^{-1} are found, while in those of (IV) and (V) there is no band at 910 cm^{-1} , but bands at 1000, 1010 and 1030 cm^{-1} are observed.

As may be seen, the result obtained is in conformity with the conclusion, drawn from ultraviolet spectra, that the synthesized hydrocarbons may be divided into two groups: those having a multiple bond conjugated with the benzene ring [(I), (II), (III) and (VI)] and those not having such conjugation [(IV) and (V)]. Comparison of spectra reveals further that the infrared spectrum of (VI) does not contain the intense bands of (I) and (II), e.g., the 925 cm^{-1} band. This excludes the possibility of the presence of an admixture of biphenyl or (II) in (VI). The existence of the above-mentioned mixtures, as well as a mixture of , is also improbable because in the case of mixtures of a conjugated compound with an unconjugated one, broadening or splitting of the C=C band at 1600 cm^{-1} should be observed. The stated arguments lead to the conclusion that the structure of (VI) should have the form , i.e., phenylcyclohexadiene-1,4. This conclusion is also in conformity with the intensities of the CH_2 group vibration bands. In Fig. 2 are shown infrared absorption spectra in the 2900-3100 cm^{-1} region for compounds (I), (III) and (VI). It is evident from this diagram that the characteristic CH_2 group band located near 2930 cm^{-1} has negligible intensity in (I) ($D < 0.01$); its optical density is 0.7 in (III) and 0.45 in (VI). It follows from this that since (III) contains four CH_2 groups, (VI) will contain about (sic) two.

On the basis of all that has been said, it may be considered that the addition of lithium to biphenyl occurs in the 3,6-position. This type of structure is in accord with Schlenk and Bergmann's finding that no anhydride is formed by the dicarboxylic acid obtained, with Hückel's observation that no adduct is formed with maleic anhydride, and with our data on the very high intensity of the 250 $\text{m}\mu$ maximum for all mono-, as well as dialkyl-dihydrobiphenyls obtained by us.

EXPERIMENTAL

1. Phenylcyclohexane was prepared through the alkylation of benzene by cyclohexanol; b.p. 100° at 5 mm, n_D^{20} 1.5250. According to cited data [7]: b.p. 115° at 15 mm, n_D^{18} 1.5264.

2. Phenylcyclohexene-1 was prepared by dehydration of phenylcyclohexanol-1 over CH_3COOH and H_2SO_4 ; b.p. 114° at 5 mm, n_D^{20} 1.5679. According to cited data [8]: b.p. 124° at 14 mm, n_D^{20} 1.5692.

3. Phenylcyclohexadiene-1,5 was prepared by a cited method [9]. To 53 g of phenylcyclohexene-1, dissolved in 100 ml of ether, 55 g of bromine was added dropwise with cooling. The reaction mass was then left for two days at room temperature. After removal of the ether the hydrocarbon was distilled and was recrystallized twice from ethanol; m.p. 54-55°. According to cited data [9]: m.p. 53-54°.

4. Preparation of phenylcyclohexene-3. Cyclohexanediol-1,4 was prepared by hydrogenation of hydroquinone in dimethylcyclohexane solution over a Raney-nickel catalyst at 110-120° and an initial hydrogen pressure of 75 atm. By slow distillation of a mixture of 15 g of the carbinol and 150 ml of hydrobromic acid, 20 g of 1,4-dibromocyclohexane was obtained. The latter was separated into cis and trans isomers by freezing. The cis isomer, 15 g of which was obtained, had b.p. 80° at 5 mm and n_D^{20} 1.5408. According to cited data [10]: b.p. 111° at 13 mm, n_D^{20} 1.5448. The trans dibromide, of which 4 g was obtained, melted at 110° after recrystallization from petroleum ether. According to cited data [11], m.p. 113°.

To the Grignard reagent prepared from 2.4 g of magnesium, 16 g of bromobenzene, and 50 ml of ether was added 24.2 g of cis-1,4-dibromocyclohexane. After boiling for 30 hours the product was worked up in the usual way. There was obtained 18 g of phenyl-4-bromocyclohexane. When the latter was boiled with alcoholic alkali, phenylcyclohexene-3 was obtained; b.p. 85° at 4 mm, n_D^{20} 1.5350. According to cited data [12]: b.p. 98° at 11 mm, n_D^{20} 1.5440.

5. Preparation of dihydrobiphenyl by addition of lithium to biphenyl. Into a flask were put 40 g of biphenyl, 300 ml of ether, and 4 g of lithium, and also glass beads. This mixture was agitated in a shaker for 100 hours, after which the reaction product was decomposed with alcohol. The ethereal solution was washed with water and dried. After removal of the solvent the liquid dihydrobiphenyl obtained was distilled in vacuo. It had b.p. 85-86° at 4 mm. After the unreacted biphenyl was frozen out, the dihydrobiphenyl had f.p. (-5°) (-6°) n_D^{20} 1.5603, d_4^{20} 0.9925. Dihydrobiphenyl did not give an adduct with maleic anhydride.

SUMMARY

On the basis of a study of the ultraviolet and infrared spectra of phenylcyclohexene-1, phenylcyclohexene-3, phenylcyclohexadiene-1,5, phenylcyclohexane, and the hydrobiphenyl obtained through the dilithium derivative of biphenyl, it has been shown that the addition of lithium to biphenyl occurs not in the 1,4-position, as Schlenk and Bergmann assumed, but in the 3,6-position.

LITERATURE CITED

- [1] W. Schlenk and E. Bergmann, *Lieb. Ann.* 463, 92 (1928).
- [2] R. Benkesser, R. Robinson, D. Souva and O. Thomos, *J. Am. Chem. Soc.* 77, 3230 (1955).
- [3] R. Benkesser, Ch. Arnold, R. Lambert and O. Thomos, *J. Am. Chem. Soc.* 77, 6042 (1955).
- [4] W. Huckel and H. Bretschneider, *Lieb. Ann.* 540, 173 (1939).
- [5] W. Huckel and R. Schwen, *Ber.* 89, 150 (1956).
- [6] A. D. Petrov, E. P. Kaplan, Z. I. Letina and Iu. P. Egorov, *J. Gen. Chem.* 28, 609 (1958). *
- [7] T. Berry and E. Reid, *J. Am. Chem. Soc.* 49, 3149 (1923).
- [8] C. Noller and G. Koneko, *J. Am. Chem. Soc.* 57, 2442 (1935).
- [9] M. Mousseron and F. Winternitz, *Bull. Soc. Chim.* (5) 12, 70 (1945).
- [10] N. D. Zelinskii and K. A. Kocheshkov, *J. Russ. Chem. Soc.* 59, 665 (1927).
- [11] A. Uspenskii and I. Tfurin, *J. Russ. Chem. Soc.* 51, 273 (1919).
- [12] C. Price and J. Karobinos, *J. Am. Chem. Soc.* 62, 2243 (1940).
- [13] R. Morton and A. de Gouveia, *J. Chem. Soc.* 916 (1934).

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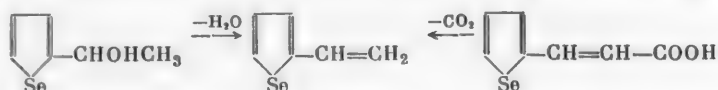
*Original Russian pagination. See C.B. Translation.

CHEMISTRY OF SELENOPHENE

XV. 2-VINYLSELENOPHENE

Iu. K. Iur'ev, N. N. Mezentsova and V. E. Vas'kovskii

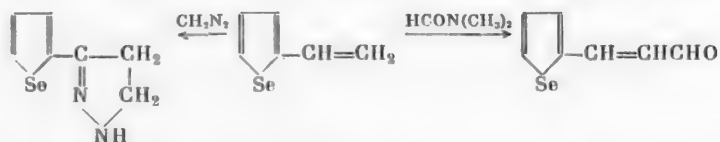
In the present work, in the course of an investigation in the field of selenophene chemistry, based on selenophene α -aldehydes [1-5], we prepared 2-vinylselenophene; of two possible routes for its synthesis, the catalytic dehydration of methyl-(selenienyl-2)-carbinol proved more convenient than the decarboxylation of β -(selenienyl-2)-acrylic acid, since it permitted the preparation of 2-vinylselenophene in considerably higher yield.



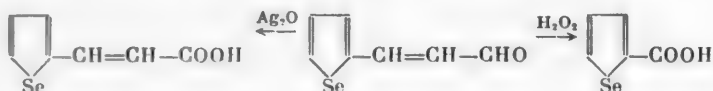
Methyl (selenienyl-2)-carbinol, as well as ethyl- and phenyl-(selenienyl-2)-carbinols, is formed smoothly by the reaction of selenophene-2-aldehyde with alkyl- and arylmagnesium halides.

On studying the effect of various dehydrating agents on methyl-(selenienyl-2)-carbinol, we found that in the presence of acidic agents — potassium bisulfate, p-toluenesulfonic acid, or an aluminosilicate cracking catalyst — or even potassium hydroxide, the 2-vinylselenophene formed is almost completely polymerized. On thermal dehydration 2-vinylselenophene is obtained in 50% yield. By vapor-phase dehydration in the presence of aluminum oxide at 200°, 2-vinylselenophene could be obtained in 80% yield. As regards the preparation of 2-vinylselenophene by the decarboxylation of β -(selenienyl-2)-acrylic acid, the attainable yield in this case is not over 40%.

On reaction with diazomethane, 2-vinylselenophene formed 4-(selenienyl-2')-pyrazoline, whereas on formylation with dimethylformamide in the presence of phosphorus oxychloride it gave β -(selenienyl-2)-acrolein



On oxidation of β -(selenienyl-2)-acrolein with silver oxide in an alkaline medium, β -(selenienyl-2)-acrylic acid was obtained; oxidation of the former with hydrogen peroxide gave selenophene-2-carboxylic acid.



EXPERIMENTAL

Methyl (selenienyl-2)-carbinol. In a three-neck flask with stirrer, reflux condenser, and dropping funnel a solution of methylmagnesium iodide was prepared from 24 g (0.17 mole) of methyl iodide and 3.65 g (0.15 mole) of magnesium in 100 ml of absolute ether with cooling (snow and salt), and to it was added 21 g (0.13 mole) of selenophene-2-aldehyde in 50 ml of absolute ether during 30-40 minutes. The reaction mixture was heated for

1 hour in a water bath, left for 12 hours, and decomposed first with water and then with 10% acetic acid. The ether extracts were dried with potash; after the ether was driven off, the residue was twice distilled in vacuo. There was obtained 19.5 g (85%).

B.p. 100-100.5° (7 mm), 98-98.5° (6 mm), n_D^{20} 1.5792, d_4^{20} 1.5294, MR_D 38.07, $C_8H_8OSeF_2$. Calculated 38.94. Found % C 40.85, 40.86; H 4.51, 4.42. C_8H_8OSe . Calculated % C 41.15; H 4.60.

Ethyl (selenienyl-2)-carbinol. In the reaction described above, ethylmagnesium bromide, prepared from 8 g (0.074 mole) of ethyl bromide and 1.7 g (0.07 mole) of magnesium in 50 ml of absolute ether, was added to 10 g (0.063 mole) of selenophene-2-aldehyde in 50 ml of absolute ether. There was obtained 10.3 g (8%).

B.p. 111-111.5° (9 mm), n_D^{20} 1.5672, d_4^{20} 1.4512, MR_D 42.55. $C_7H_{10}OSeF_2$. Calculated 43.56. Found % C 44.12, 44.28; H 5.06, 5.21. $C_7H_{10}OSe$. Calculated % C 44.46; H 5.33.

Phenyl (selenienyl-2)-carbinol. Phenylmagnesium bromide, prepared from 11 g (0.07 mole) of bromobenzene and 1.7 g (0.07 mole) of magnesium in 50 ml of absolute ether, was made to react with 10 g (0.063 mole) of selenophene-2-aldehyde in 50 ml of absolute ether. There was obtained 9.6 g (64.5%).

B.p. 182-183° (9 mm); m.p. 60.61° (from ligroin); colorless crystals. Found % C 55.96, 55.99; H 4.52, 4.59. $C_{11}H_{10}OSe$. Calculated % C 55.71; H 4.25.

2-Vinylselenophene. a) Ten g (0.05 mole) of β -(selenienyl-2)-acrylic acid (m.p. 114° [1]) and a small amount of phenyl- β -naphthylamine were slowly heated in a Wurtz flask in an oil bath at 180-200° in a current of nitrogen. The 2-vinylselenophene which distilled off was washed with water and dissolved in 10-15 ml of ether. The ethereal solution was dried with calcium chloride. After the ether was driven off, the residue was distilled in vacuo in a current of nitrogen. There was obtained 3.1 g (40%). 2-Vinylselenophene, obtained from a series of experiments, had the following constants after redistillation.

B.p. 95-95.5° (81 mm), 77-77.5° (40 mm), 69.5-70° (25 mm), n_D^{20} 1.6115, d_4^{20} 1.4460, MR_D 37.72. $C_6H_6SeF_3$. Calculated 36.95.

The residue in the flask was a dark, tarry mass.

b) A solution (35%) of methyl (selenienyl-2)-carbinol in benzene, containing a small amount of phenyl- β -naphthylamine, was heated and, at 30-40 mm pressure in a weak current of nitrogen, was passed through a tube (inner diameter 10 mm) filled with pieces of aluminum oxide (length of layer, 35 cm). The catalyzate was collected in a cooled receiver, and after the benzene (along with water) was driven off in a current of nitrogen, the residue was distilled in vacuo. The results obtained are given in the table.

In 6 hours without catalyst at 100°, 2-vinylselenophene polymerizes relatively slowly, being converted to a viscous, dark-red liquid.

Peroxides (benzoyl peroxide and hydrogen peroxide), and also potassium hydroxide, have a slight effect on the rate of polymerization on heating for 1 and 6 hours.

On heating for 1 hour in the presence of hydrochloric acid, vinylselenophene is converted to a viscous, dark-brown liquid; on heating for 6 hours, the product is a soft, dark-brown plastic.

4-(Selenienyl-2')-pyrazolinium oxalate. To a solution of 5.5 g (0.035 mole) of 2-vinylselenophene in 100 ml of absolute ether was added 200 ml of an ethereal solution of diazomethane [from 7.2 g (0.07 mole) of nitrosomethylurea], and the reaction mixture was heated for 12 hours in a water bath. After most of the ether was distilled off in vacuo, a saturated ethereal solution of anhydrous oxalic acid was added to the residue (~50 ml). There was obtained 4.5 g (53%); m.p. 113-114°.

Found % C 39.16, 39.10; H 3.70, 3.75; N 11.07, 11.15. $C_{16}H_{18}O_4N_4Se_2$. Calculated % C 39.40; H 3.72; N 11.45.

β -(selenienyl-2)-acrolein. To 7.13 g (0.10 mole) of dimethylformamide in a three-neck flask with stirrer, reflux condenser, and dropping funnel at 5° was added 15.2 g (0.10 mole) of phosphorus oxychloride. The mixture was stirred for 15 minutes at 20°, after which 35 ml of dichloroethane was poured in; then, at 5°, a solution of 14.2 g (0.096 mole) of 2-vinylselenophene in 35 ml of dichloroethane was slowly added. After heating in a water bath for 15 minutes the mixture was cooled, and a solution of 75 g of sodium acetate in 120 ml of water was added; the mixture was heated almost to boiling and cooled. The dichloroethane layer was drawn off, and the water layer was extracted with ether; after drying with anhydrous sodium sulfate and driving off the solvents the residue was distilled in vacuo in a current of nitrogen. There was obtained 9.2 g (55%).

Quantity of methyl (selenienyl-2)-carbinol (in g)	Quantity of benzene (in ml)	Temperature of experiment	Rate of introduction of the mixture (ml/min)	Yield of 2-vinylselenophene	
				(in g)	(in %)
5	15	300-305°	1.5	2.5	56
10	30	250-255	1.5	7.1	80
5	15	210-215	1.2	3.5	78
5	15	215-220	3.5	3.4	76
5	15	155-160	1.0	3.0	67
5	15	110-115	1.2	1.2	27

B.p. 155-155.5° (15 mm), 148-149° (9 mm), n_D^{20} 1.7006, d_4^{20} 1.5495, MR_D 46.13. $C_7H_6OSeF_3$. Calculated 41.59.

Found %: C 45.25, 45.33; H 3.36, 3.41. C_7H_6OSe . Calculated %: C 45.42; H 3.21.

β -(Selenienyl-2)-acrolein semicarbazone was prepared from 0.75 g of the aldehyde in 4 ml of alcohol, 0.75 g of semicarbazide hydrochloride, and 1.2 g of sodium acetate; m.p. 213-214° (decomp., from 90% alcohol).

Found %: N 17.26, 17.22. $C_8H_9ON_3Se$. Calculated %: N 17.35.

β -(Selenienyl-2)-acrolein thiosemicarbazone was prepared from 1 g of the aldehyde in 10 ml of alcohol, 0.5 g of thiosemicarbazide hydrochloride, and 0.1 ml of glacial acetic acid; m.p. 146-147° (from alcohol).

Found %: N 16.09, 16.02. $C_8H_9N_3SSe$. Calculated %: N 16.26.

β -(Selenienyl-2)-acrylic acid. To a mixture of 0.5 g of β -(selenienyl-2)-acrolein and 0.3 g of sodium hydroxide in 10 ml of water, alcohol was added until the aldehyde dissolved, and a saturated aqueous solution of 1 g of silver nitrate was then added dropwise. After standing for a day, filtration, concentration of the filtrate, and acidification with concentrated hydrochloric acid, 0.49 g (90%) of the acid was obtained; m.p. 139-140° (from water); a mixture test with known β -(selenienyl-2)-acrylic acid [1] showed no depression.

Selenophene-2-carboxylic acid. To 20 ml of 5% sodium hydroxide solution at 60° was added 1 g of β -(selenienyl-2)-acrolein and 15 ml of 3% hydrogen peroxide; the reaction mixture was acidified (to litmus) with concentrated hydrochloric acid and extracted with ether. After the ether was distilled off, 0.76 g (80%) of the acid was obtained; m.p. 119.5-120° (from water); a mixture test with known selenophene-2-carboxylic acid [1] showed no depression.

SUMMARY

1. The reaction of selenophene-2-aldehyde with alkyl- and arylmagnesium halides leads to the formation of secondary alcohols of the selenophene series. Methyl-, ethyl-, and phenyl (selenienyl-2)-carbinols, prepared in this way, are described for the first time.
2. The catalytic dehydration of methyl (selenienyl-2)-carbinol and the decarboxylation of β -(selenienyl-2)-acrylic acid both lead to 2-vinylselenophene.
3. The reaction of 2-vinylselenophene with diazomethane leads to the formation of 4-(selenienyl-2'-)pyrazoline.
4. On formylation of 2-vinylselenophene with dimethylformamide, β -(selenienyl-2)-acrolein is obtained.

LITERATURE CITED

- [1] Iu. K. Iur'ev and N. N. Mezentsova, J. Gen. Chem. 27, 179 (1957).*
- [2] Iu. K. Iur'ev, N. N. Mezentsova and T. A. Balashova, J. Gen. Chem. 27, 2536 (1957).*
- [3] Iu. K. Iur'ev, N. N. Mezentsova and V. E. Vas'kovskii, J. Gen. Chem. 27, 3155 (1957).*
- [4] Iu. K. Iur'ev and N. N. Mezentsova, J. Gen. Chem. 28, 3041 (1958).*
- [5] Iu. K. Iur'ev and N. K. Sadovala and M. A. Gal'bershtam, J. Gen. Chem. 28, 620 (1958).*

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DECOMPOSITION OF LIGNIN BY METALLIC SODIUM IN LIQUID AMMONIA

VII. CHROMATOGRAPHIC INVESTIGATION OF THE PHENOLS OBTAINED IN THE DECOMPOSITION OF LIGNIN

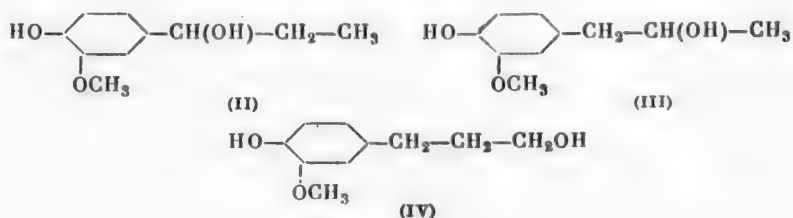
A. F. Semechkina and N. N. Shorygina

Earlier we established that metallic sodium in liquid ammonia solution decomposes lignin with the formation of monomeric phenols [1-3]. From the decomposition products of the copper-ammonia and hydrochloric acid lignins of spruce wood there were isolated dihydroeugenol and the phenolic alcohol $C_{16}H_{14}O_3$. The latter was obtained in the form of a sirup which gave a bis-phenylurethane and a dibenzoate; however, these had unsharp melting points. On oxidation of the sirup vanillic acid was obtained. It was suggested that the sirupy product contains 1-(4-hydroxy-3-methoxyphenyl)-propanol-1 or -2.

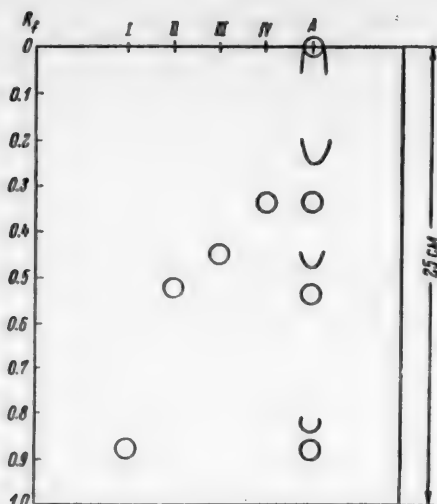
For a more detailed study of the phenolic decomposition products of lignin, formed by treatment of spruce-wood lignin with a solution of sodium in ammonia, paper chromatography was used. The lignin was prepared from wood according to the existing methods of Freudenberg [4] and Willstätter [5]. Treatment with a solution of sodium in liquid ammonia was carried out under the conditions described earlier [1], but with this modification: after the products of treatment of the lignin were decomposed with moist ether and with water, the aqueous, alkaline solution was not extracted with ether (to isolate dihydroeugenol), but was quickly acidified with dilute sulfuric acid, and only the acid solution was subjected to ether extraction. The mixture of phenols, thus obtained, was separated from acids by ether extraction from bicarbonate solution.

The purified sirupy mixture of phenols was chromatographed on paper by the descending method. The following solvents were used: 1) petroleum ether-benzene-water in the ratios 1:1:1; 2) petroleum ether-benzene-acetic acid-water in the ratios 1:1:0.25:1; 3) ligroin saturated with water. The phenols were developed with diazotized sulfanilamide. "Crab" (base under parchment) paper was used.

The composition of the phenols proved to be quite complex. On the chromatogram the lilac-colored spot of dihydroeugenol (I) is situated lowest of all (see diagram). Above it are the 1-(4-hydroxy-3-methoxyphenyl)propanols, of which all three possible isomers, guaiacyl-n-propanols-1, -2, and -3 (I, II, III), were found to be present.



The spot of substance (II), corresponding in position to the synthesized control substance, has an intense, rosy-orange color, whereas that of (IV) has a bright-lilac hue, corresponding to the color formed by synthesized substance (IV). The spot of (III), situated between those of (II) and (IV), is indistinct and has only a pale-lilac tint, while synthetic phenol alcohol (III) gives a bright-lilac spot in the same position. Above the spots for the group of the stated phenolic alcohols on the chromatogram of spruce-wood phenols, there are bright-orange spots, the nature of which has not yet been ascertained.



Paper chromatogram. Disposition of phenols from the hydrochloric-acid lignin of spruce wood.

I) Dihydroeugenol; II) 1-(4-hydroxy-3-methoxyphenyl)propanol-1; III) 1-(4-hydroxy-3-methoxyphenyl)propanol-2; IV) 1-(4-hydroxy-3-methoxyphenyl)propanol-3; A) phenolic mixture from lignin.

The presence in lignin of side-chains with a hydroxyl group in the α -position with respect to the benzene nucleus (benzyl alcohol groups) has recently been indirectly proved several times by various investigators. A number of authors base their conclusion that these groups are present, on the sulfiting, and also the sulfiding, of lignin and type compounds [9]. Adler and Gierer [10] reach this conclusion by studying the methylation of lignin and type compounds by $\text{CH}_3\text{OH} + \text{HCl}$ at room temperature; the quantity of structural elements with free and etherified OH groups in the α -position with respect to the nucleus was estimated by the authors to be 50% of the total number of phenylpropane monomers for Braun's lignin.

Gierer [11], combining Braun's lignin with quinonemonochloroimine, concludes that in this lignin there must be one free group of the *p*-hydroxybenzyl alcohol type attached to every 7,8-phenylpropane link.

Use of the method of decomposition of lignin by sodium permitted a direct proof of the presence of these substances.

EXPERIMENTAL

1. Decomposition of lignin by sodium in liquid ammonia. Lignin, obtained by the hydrochloric acid method, had the composition (in %): C 62.81; H 6.05; OCH_3 15.20. Fifteen g of lignin was treated with 11.25 g of Na in liquid ammonia under the conditions used by us earlier. After decolorization of the blue solution (9 days) and removal of the ammonia, moist ether was added to the reaction vessel. Then, in a current of nitrogen, water was added, followed by dilute sulfuric acid until an acid reaction (with Congo) was obtained. The solution was extracted with ether. The phenols were separated from acids by ether extraction from a bicarbonate solution. Yield of phenols, 0.5 g. The phenols obtained were chromatographed.

2. Paper chromatography. On a 15 × 30 cm strip of ("Crab") paper, a spot consisting of an alcoholic solution of the phenols being investigated was placed at a distance of 4 cm from the edge, alongside spots of solutions of known monomers (I-IV) and developed for 6-12 hours with a moist mixture of benzene and petroleum ether (1:1 by volume) by the descending method. Then the strips were sprayed with a solution of diazotized

In order to determine the behavior of the phenolic alcohols thus found, under the conditions of the decomposition of lignin, compounds (II), (III) and (IV) were treated with a solution of sodium in liquid ammonia under the conditions which we used for decomposing lignin.

The phenols which were isolated from the reaction mixture (after its decolorization) proved to be mainly the initial substances, with a very slight admixture of dihydroeugenol. On treatment with sodium in liquid ammonia solution, guaiacylacetone was quantitatively reduced to (III). Coniferyl alcohol gave dihydroeugenol in almost quantitative yield, as we had shown earlier [1].

Thus, under the conditions which we used for decomposing lignin, ketone groups in position 2 of the chain are not retained. However, considering that the yield of substance (III) from lignin is negligible, it may be assumed that there can only be very few CO groups in this position in lignin.

It might be mentioned that dihydroeugenol was repeatedly obtained from lignin in small quantities, e.g., in approximately 0.5% yield (based on the lignin taken), on dry distillation of corn husks in a hydrogen atmosphere in vacuo [6] and on heating sulfite caustics with alkali [7].

Phenol alcohol (IV) was found by paper chromatography in the ether-soluble fraction of maple hydro-lignin [8].

sulfanilamide in butyl alcohol and dried, after which they were sprayed with a semisaturated soda solution. The phenols were revealed in the form of colored spots.

3. Synthesis of monomers. 1-(4-Hydroxy-3-methoxyphenyl)propanol-1 was prepared by a cited method [12] through the reaction of vanillin (10 g) with ethylmagnesium bromide. Yield 8 g, m.p. 86° (from benzene), which corresponds to cited data [12].

Found %: C 65.78; H 7.91. $C_{10}H_{14}O_3$. Calculated %: C 65.93; H 7.69.

1-(4-Hydroxy-3-methoxyphenyl)propanol-3 was prepared by the reduction of ethyl hydroferulate with lithium aluminum hydride. Four g of the hydroferulic acid ester, dissolved in absolute ether (200 ml), were added dropwise to 4 g of lithium aluminum hydride, also dissolved in absolute ether (200 ml), during 1 hour with stirring, after which stirring was continued for 2 more hours. Then the reaction mass was discharged dropwise into ice. After acidification the carbinol was extracted with ether. M.p. 65°, yield 3.5 g.

Found %: C 65.71; H 7.74. $C_{10}H_{14}O_3$. Calculated %: C 65.93; H 7.69.

1-(4-Hydroxy-3-methoxyphenyl)propanone-2 was prepared by condensation of vanillin with nitroethane and subsequent reduction of the 4-hydroxy-3-methoxy- β -nitropropenyl-1-benzene obtained (1.6 g), by a cited method [13]. B.p. 155° (4 mm), yield 0.6 g.

1-(4-Hydroxy-3-methoxyphenyl)propanol-2* was prepared by reduction of the propanone-2 with lithium aluminum hydride, M.p. 52°.

4. Carrying out the reactions of monomers with metallic sodium in liquid ammonia.

a) To a solution of 1.75 g of coniferyl alcohol in 200 ml of liquid ammonia was added 1.75 g of metallic sodium. The reaction was continued for a week, the reaction mass being cooled with dry ice. Part of the sodium did not react during the stated period. The ammonia was removed by evaporation, and the mass left in the vessel was covered with moist ether and acidified with dilute sulfuric acid. From the ether extract, 1.5 g of an oily liquid was obtained. A chromatogram revealed the presence of dihydroeugenol together with a faint spot of 1-(4-hydroxy-3-methoxyphenyl)propanol-3.

b) 1-(4-Hydroxy-3-methoxyphenyl)propanol-1 was subjected to the same conditions. Chromatography revealed the presence of unchanged 1-(4-hydroxy-3-methoxyphenyl)propanol-1. There was also a faint spot of dihydroeugenol.

c) On the chromatogram, obtained after treatment of 1-(4-hydroxy-3-methoxyphenyl)propanol-3 with sodium in liquid ammonia, there was an intense spot of the original carbinol and a faint spot of dihydroeugenol.

d) One g of 1-(4-hydroxy-3-methoxyphenyl)propanone-2 was dissolved in 150 ml of liquid ammonia, and 1 g of sodium was added. The reaction was continued for 4 days, the reaction mass being cooled with dry ice. All the sodium reacted. The chromatogram showed the presence only of 1-(4-hydroxy-3-methoxyphenyl)propanol-2.

SUMMARY

On decomposition of spruce lignin by metallic sodium in liquid ammonia there is obtained a mixture of phenols, of which dihydroeugenol and 1-(4-hydroxy-3-methoxyphenyl)propanols-1 and -3 were identified through paper chromatography.

Part of the phenols obtained on decomposition of spruce lignin have not yet been identified.

LITERATURE CITED

- [1] N. N. Shorygina, T. Ia. Kefeli and A. F. Semechkina, J. Gen. Chem. 19, 1558 (1949).*
- [2] N. N. Shorygina and T. Ia. Kefeli, J. Gen. Chem. 20, 1199 (1950). **
- [3] N. N. Shorygina, T. Ia. Kefeli and A. F. Semechkina, Proc. Acad. Sci. USSR 64, 689 (1949).

*First synthesized by A. A. Chuksanova.

**Original Russian pagination. See C. B. Translation.

- [4] Freudenberg, Harder and Markett, Ber. 61, 1762 (1928); Freudenberg and Zocher, Ber. 62, 1814 (1929).
- [5] Willstätter and Kalb, Ber. 55, 2637 (1922).
- [6] Phillips and Goss, J. Am. Chem. Soc. 54, 1518 (1932); Phillips, J. Am. Chem. Soc. 53, 768 (1931).
- [7] Zedlinski and Sawlewicz, Przem. Chem. 11, 9, 568 (1953).
- [8] Granath and Schurach, J. Am. Chem. Soc. 75, 707 (1953).
- [9] M. Hiroshi, Bull. Chem. Soc. 27, 59 (1954); Heden and Holmberg, Svensk. Kem. Tidn. 48, 207 (1936); Lindgren, Acta Chem. Scand. 3, 1011 (1949); 6, 963 (1952); Erdtman and Leopold, Acta Chem. Scand. 3, 1358 (1949); Enkvist and Moilanen, Svensk. Papperstidn. 52, 183 (1949); Lindgren, Acta Chem. Scand. 4, 1365 (1950); Lindgren, Svensk. Papperstidn. 55, 78 (1952); Lindgren, Acta Chem. Scand. 5, 603 (1951); Adler and Yllner, Svensk Papperstidn. 55, 238 (1952); Adler, Lindgren and Saldin, 55, 245 (1952); Adler and Yllner, 57, 78 (1954).
- [10] Adler and Gierer, Acta Chem. Scand. 9, 84 (1955).
- [11] Gierer, Acta Chem. Scand. 8, 1319 (1954).
- [12] Roberti, Lork, Warren and McGregor, J. Am. Chem. Soc. 72, 5760 (1950).
- [13] M. Kulka and H. Hibbert, J. Am. Chem. Soc. 65, 1180 (1943).

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ON THE MECHANISM OF ACTION OF ACCELERATORS OF THE PROCESS OF SULFUR VULCANIZATION

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It was shown earlier that some accelerators of sulfur vulcanization, in particular ethanolamine, ethylene diamine and its derivatives, glucose and fructose, react with sulfur at 100-160° with the formation of hydrogen sulfide [1]. In connection with the postulated role of hydrogen disulfide as an intermediate product in this reaction its decomposition in solution in alkylbenzenes and olefins has been studied and it was shown that the process proceeds by a chain mechanism in which HS^\cdot and HS_2^\cdot radicals take part [2, 3]. In cumene, ethylbenzene and similar solvents the decomposition of H_2S_2 results in the formation of equivalent amounts of hydrogen sulfide and sulfur. In solution in α -olefins, which are effective free-radical acceptors, the formation of hydrogen sulfide is suppressed and the reaction products are mono-, di- and tetrasulfides. In β -olefins considerable amounts of hydrogen sulfide and sulfur are present in the reaction products in addition to the sulfides mentioned [2, 3].

In order to elucidate the mechanism of action of vulcanization accelerators it was necessary to study the composition of the products formed by their interaction with sulfur in various solvents and to compare it with the composition of the decomposition products of H_2S_2 in the same solvents. For this purpose we studied the reaction of monoethanolamine, ethylene diamine and fructose with sulfur in pentenes-1 and -2, cyclohexene, isoprene, α -methylstyrene, styrene, ethylbenzene and a rubber solution, at 130-160°. The process was characterized by the yield of hydrogen sulfide, and in the case of the reaction of monoethanolamine with sulfur in pentenes-1 and -2, all the main reaction products were isolated and characterized. Table 1 shows the data on the yield of hydrogen sulfide from the interaction of sulfur with the vulcanization accelerators and also from the decomposition of hydrogen disulfide in various solvents.

From the data presented in Table 1 it is seen that the yield of hydrogen sulfide from the interaction of monoethanolamine, ethylene diamine and fructose with sulfur in ethylbenzene is near to the theoretical in a number of cases. On conducting the reaction in α -olefins or rubber solution the yield of hydrogen sulfide falls to 0. In β -olefins, the double bond of which is less reactive towards free radicals [4], 20-40% of the theoretical amount of H_2S is evolved. Similar results are obtained for the decomposition of hydrogen disulfide.

In Table 2 experimental results are presented for the composition of the reaction products of sulfur and monoethanolamine in solution in pentenes-1 and -2. Here again the results of experiments on the decomposition of hydrogen disulfide are presented for comparison.

From the data of Table 2 it is seen that the interaction of sulfur with the vulcanization accelerators in an olefinic medium and also the decomposition of H_2S_2 in olefins, results in the formation of saturated sulfides. The yields of diamylmonosulfide from the reaction in pentene-1 (29%) and in pentene-2 (13%) are in good agreement with the yields of the monosulfide from the decomposition of H_2S_2 in the same solvents. The yields of diamyldisulfide in the products from the reaction of sulfur with the accelerator both in pentene-1 (30%) and in pentene-2 (9%) are higher than those from the decomposition of H_2S_2 . There are substantial differences also in the yields of diamyltetrasulfide. In the reaction product in pentene-2 the yield of the tetrasulfide is 8% as against 19% for the decomposition of H_2S_2 .

The comparatively low yields of tetra- and polysulfides in the cases examined is explained by the presence in the system of a considerable quantity of compounds with sulfhydryl groups (mercaptans, H_2S , H_2S_2). As is known, free aliphatic radicals react quantitatively with sulfur to form the corresponding polysulfides.



TABLE 1

Yield of H_2S on Reaction of Sulfur with Vulcanization Accelerators and from the Decomposition of H_2S_2 in Various Solvents

Concentration of sulfur 0.315 g atoms/liter. Ratio of components: 1 atom of S per mole of accelerator. Concentration of H_2S_2 1.01-1.18 g moles/liter

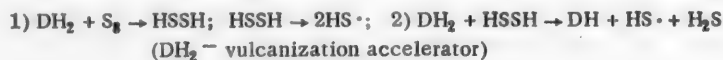
Solvent	Reagent	Temperature	Reaction time	Yield of H_2S^* (in %)
Ethylbenzene	Ethylenediamine + S	140°	1	30.0
		140°	8	66.5
	Fructose + S	160	8	48.5
	Monoethanolamine + S	143	1	38.8
		143	9	97.7
5% solution of SKS-30 rubber in ethylbenzene	H_2S_2	70	12	98.0
	Ethylenediamine + S	140	1	0**
		140	5	0**
	Fructose + S	160	1	0**
		160	5	0**
α -methylstyrene	Monoethanolamine + S	140	1	0**
		140	5	0**
	H_2S_2	70	15	0**
	Ethylenediamine + S	140	8	0
		160	10	0
Styrene	Fructose + S	140	6	0
	H_2S_2	70	1	5.0
		70	5	5.0
Pentene-1	Monoethanolamine + S	130	10	0
		130	10	5.2
	H_2S_2	50	15	9.2
Pentene-2	Monoethanolamine + S	130	10	41
	H_2S_2	50	15	42
Cyclohexene	Monoethanolamine + S	130	10	23
		50	15	58

When sulfur is present at the same time as mercaptans or hydrogen sulfide, of the two concurrent reactions: 1) $R \cdot + S_8 \rightarrow RS_{7.5}R$ and 2) $R \cdot + R'SH (H_2S, H_2S_2) \rightarrow RH + R'S \cdot (HS \cdot, HS_2 \cdot)$, the second takes place preferentially [5]. The absence of mercaptans from the reaction products conforms with the fact that reaction 2 proceeds considerably more rapidly than reaction 1.

It should be noted that under the given reaction conditions hydrogen sulfide does not add on to double bonds in the absence of free radicals [6], and sulfur reacts with olefins only to a small extent, forming higher polysulfides [7, 8].

The formation of the products obtained can be explained only by assuming that $HS \cdot$ and $HS_2 \cdot$ radicals take part in the process [3].

The initial active centers are produced as a result of the reaction:



* In the case of the decomposition of hydrogen disulfide the quantity of H_2S formed according to the reaction $H_2S_2 \rightarrow H_2S + \cdot S$ was taken as theoretical.

** Gel formation.

TABLE 2

Composition of Products from Reaction of Sulfur with Monoethanolamine and Decomposition Products of H_2S_2 in Pentenes-1 and -2.

Olefin	System	Temperature	Sulfur content in product (in % of initial)				
			H_2S	$(\text{C}_2\text{H}_5)_2\text{S}$	$(\text{C}_2\text{H}_5)_3\text{S}_2$	$(\text{C}_2\text{H}_5)_4\text{S}_3$	$(\text{C}_2\text{H}_5)_n\text{S}_n + \text{S}$
Pentene-1	Monoethanolamine + sulfur H_2S_2	130°	0	29	30	—	17.7
		130	2.6	31	16.5	19.0	23.0
		50	4.6	31—39	11.8	25	18
Pentene-2	Monoethanolamine + sulfur H_2S_2	130	40.8	13.2	9	7.8	5
		50	21.0	15	3	19	31

The role of the latter reaction is evidently small because in the presence of olefins only insignificant quantities of hydrogen sulfide are formed. The comparatively small yield of polysulfides provides evidence against the possibility of formation of significant quantities of HS_2H in reaction 1.

Hence the system consisting of sulfur and one of the vulcanization accelerators examined is a particular case of an oxidation-reduction initiated, radical process. In this case the oxidizing agent is sulfur and the reducing agents — the amines, hydroxycarbonyl, and certain other compounds.

The formation of hydrogen sulfide in the reaction between sulfur and vulcanization accelerators in ethylbenzene and other, similar solvents is evidently connected only with disproportionation of the free radicals $\text{HS} \cdot$ and $\text{HS}_2 \cdot$ because hydrogen sulfide and sulfur are formed in equimolecular quantities on decomposition of H_2S_2 in these solvents [3]. The latter indicates that the $\text{HS} \cdot$ radical is unable to abstract hydrogen from the solvent. These radicals are very active in addition reactions to the double bonds of olefins, α -olefins being considerably more active than β -olefins. Hence the rules established in relation to the reactivity of internal and terminal double bonds towards aliphatic radicals, are confirmed also in the case of radicals with the active center on a sulfur atom.

EXPERIMENTAL

Pentene-1 was prepared from ethyl bromide and allyl bromide [9], b.p. 30°, n_D^{20} 1.3720.

Pentene-2 was prepared by dehydration of secondary amyl alcohol [10], b.p. 35.5° (736 mm), n_D^{20} 1.3790.

Cyclohexene was prepared by dehydration of cyclohexanol [11], b.p. 83.5°, n_D^{20} 1.4453.

The reaction between sulfur and monoethanolamine in solution in olefins was carried out in sealed ampoules in an atmosphere of dry nitrogen. The ampoule containing a weighed quantity of sulfur was evacuated a few times on an oil pump and the vacuum was let down with nitrogen. Weighed quantities of monoethanolamine and solvent were added against a countercurrent of nitrogen. The sealed ampoules were heated in an air thermostat at 130° with continuous shaking for 10 hours. At the end of the heating period the ampoules were cooled to -70°, opened and connected to a system for the absorption of hydrogen sulfide (CdCl_2 solution). For this purpose a current of nitrogen was passed through the solution at 0° and the CdS formed was determined iodometrically [12]. Divided portions of the solution after removal of H_2S were analyzed for mercaptan content.

The reaction mixture obtained consisted of a solution of sulfides in the olefin and a dark-red, resinous precipitate, soluble in water. The olefin solution of sulfides was decanted from the precipitate and treated as described in [3]. The precipitate was dissolved in water and analyzed for H_2S content (by reaction with AgNO_3) and for total sulfur content (by oxidation with bromine with subsequent precipitation of SO_4^{2-} as BaSO_4).

Interaction of sulfur with monoethanolamine in pentene-1. 1.0 g of sulfur, 2.1 g of monoethanolamine and 35 ml of pentene-1 were taken. Concentration of S, 0.895 g atoms / liter. H_2S was not found in the reaction products.

The following were isolated: a) diamylmonosulfide 1.43 g (28.0% of initial sulfur)

B.p. 89-90° (12-13 mm), d_4^{15} 0.8452, n_D^{15} 1.4568.

Found % C 68.66; H 11.54; S 19.47; monosulfide sulfur 98.8. Iodine number 0. M 164.177. $C_{10}H_{22}S$.
Calculated % C 68.96; H 12.64; S 18.39. M 174.

b) Diamyldisulfide 1.0 g (30% of initial sulfur).

B.p. 120-124° (12-13 mm), d_4^{15} 0.9620, n_D^{15} 1.5003.

Found % C 62.11; H 10.12; S 30.0; disulfide sulfur 97.0. Iodine number 0, M 207.201, $C_{10}H_{22}S_2$.
Calculated % C 58.25; H 10.68; S 31.07. M 206.

c) The residue after removal of the mono- and disulfides by distillation, consisting of a mixture of polysulfides, was dissolved in toluene and refluxed with sodium sulfate solution for the determination of polysulfides and free sulfur [13]. The content of disulfide sulfur in the solution, after removal of free sulfur, was determined. The total quantity of sulfur found on analysis of the precipitate was 17.7% (including 7.7% disulfide sulfur).

d) In the hydrocarbon-insoluble residue from the ampoule ("resin") 14.0% of the initial sulfur was found after oxidation with bromine. The residue did not contain hydrogen sulfide.

The over-all sulfur balance of the products was 90%.

Interaction of sulfur with monoethanolamine in pentene-2. 2 g of sulfur and 4.2 g of monoethanolamine were taken. Concentration of S, 1.25 g atoms/liter.

The following were isolated: a) H_2S (gaseous and from the resin) 0.448 g (40.8%).

b) Diamylmonosulfide 1.39 g (13.2% of initial S).

B.p. 54-55° (2-3 mm), d_4^{15} 0.8428, n_D^{15} 1.4574.

Found % C 68.10; H 12.57; S 18.46; monosulfide sulfur 101. Iodine number 0. M 168.5, 170.2. $C_{10}H_{22}S$. Calculated % C 68.96; H 12.64; S 18.39. M 174.

c) Diamyldisulfide 0.57 g (9% of initial S).

B.p. 90° (2 mm), n_D^{15} 1.5056.

Found % C 59.37; H 9.88; S 30.75; disulfide sulfur 95. Iodine number 0. M 201. $C_{10}H_{22}S_2$. Calculated % C 58.25; H 10.68; S 31.07. M 206.

d) Diamyltetrasulfide 0.31 g (7.7% of initial S), b.p. 120-130° (2 mm).

Found % C 46.47; H 7.91; S 46.02. $C_{10}H_{22}S_4$. Calculated % C 44.44; H 8.15; S 47.70.

e) 5% of the sulfur was found in the residue after fractionation (including 1% disulfide sulfur).

f) In the "resin," in addition to hydrogen sulfide (20.8%), 9% of the initial sulfur was found.

SUMMARY

1. It is shown that the reaction of sulfur with various reducing agents that act as accelerators of the sulfur vulcanization process, proceeds through the intermediate stage of hydrogen disulfide, which decomposes with formation of $S\cdot$ and $S_2\cdot$ radicals.

2. On the basis of a study of the composition of the products formed by the interaction of sulfur with vulcanization accelerators and in the decomposition of hydrogen disulfide, in α - and β -olefins a suggestion is made about the mechanism of the formation of sulfur bonds in the vulcanization process and the role of accelerators in this process.

3. It is shown that terminal double bonds are considerably more reactive towards $HS\cdot$ and $HS_2\cdot$ radicals than are internal double bonds. It is shown that $HS\cdot$ radicals at 130° do not abstract hydrogen from aliphatic hydrocarbon solvents.

LITERATURE CITED

- [1] E. I. Tiniakova, E. K. Khrennikova, B. A. Dolgoplosk, V. N. Reikh and T. G. Zhuravleva, *J. Gen. Chem.* 26, 2476 (1956).*
- [2] E. I. Tiniakova, E. K. Khrennikova and B. A. Dolgoplosk, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 1152 (1956). *
- [3] E. I. Tiniakova, E. K. Khrennikova and B. A. Dolgoplosk, *J. Gen. Chem.* 28, 1632 (1958). *
- [4] E. B. Milovskaya, B. A. Dolgoplosk and B. L. Erusalimskii, *Proc. Acad. Sci. USSR*, 120, 336 (1958). *
- [5] E. I. Tiniakova, B. A. Dolgoplosk and M. P. Tikhomolova, *J. Gen. Chem.* 25, 1387 (1955). *
- [6] Mayo and Walling, *Chem. Revs.* 27, 387 (1940).
- [7] Armstrong, Little and Doak, *Ind. Eng. Ch.* 36, 628 (1944).
- [8] Meyer and Hohenemser, *Helv. Chim. Acta.* 18, 1061 (1935).
- [9] B. A. Kazanskii, A. L. Liberman and A. F. Plate, *J. Gen. Chem.* 17, 1503 (1947).
- [10] *Syntheses of Organic Preparations*, I, 335 (1949). **
- [11] *Organic Syntheses*, I, 183 (1948).
- [12] Bell and Agruss, *Ind. Eng. Chem.* 13, 297 (1941).
- [13] V. V. Gurova and B. V. Bolotnikov, *J. Rubber Ind. No.* 6, 61 (1933).

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**In Russian.

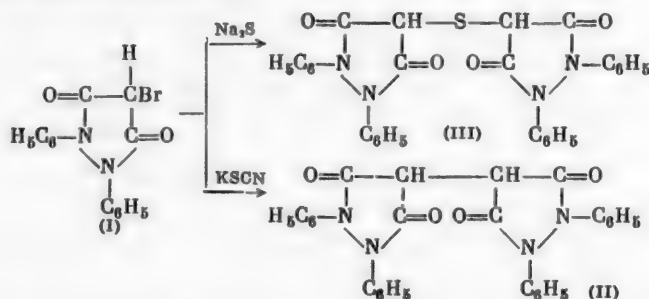
INVESTIGATIONS IN THE FIELD OF THE CHEMISTRY OF PYRAZOLIDINE

V. ON SOME ANOMALOUS REACTIONS OF 1,2-DIPHENYL-3,5-DIOXOPYRAZOLIDINE AND ITS HALOGEN AND THIOCYANOGEN DERIVATIVES

V. G. Pesin, A. M. Khaletskii and Teng Jun-hsiang

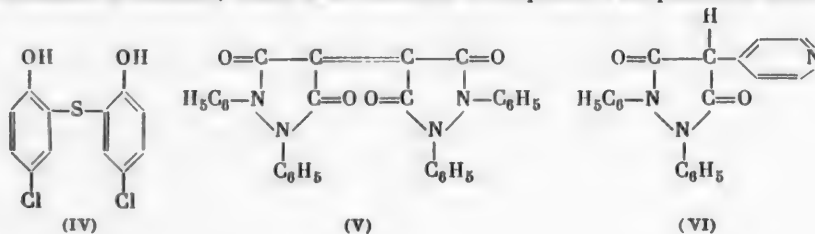
1,2-Diphenyl- and 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidines and their halogen and thiocyanogen derivatives take part anomalously in certain reactions. It has already been reported [1] that on reacting 4-n-butyl-4-thiocyano-1,2-diphenyl-3,5-dioxopyrazolidine with alcoholic alkali, a substance containing no sulfur, and not the disulfide, is formed. Some anomalous reactions of 1,2-diphenyl-3,5-dioxopyrazolidine and its 4-bromo derivative are discussed in this communication.

On reacting 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine (I) with potassium thiocyanate, 4-thiocyano-1,2-diphenyl-3,5-pyrazolidine is not formed but 4,4-bis-(1,2-diphenyl-3,5-pyrazolidine) (II), the structure of which we proved by independent synthesis (interaction of bismalonic ester and hydrazobenzene). Compound (II), as reported previously [1], is formed as a by-product together with the main product - bis-(1,2-diphenyl-3,5-dioxopyrazolidine) sulfide (III) - on reacting 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine (I) with sodium sulfide or with triethylammonium diethylthiophosphate.



Comparison of these reactions (interaction of (I) with sodium sulfide and with potassium thiocyanate) suggests that the formation of (II) proceeds by a radical mechanism. The results obtained in attempts to carry out reactions between 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine (I) with p-chlorophenol or with 2,2'-dioxo-5,5'-dichlorodiphenyl sulfide (IV) seem to us to be anomalies of the same type.

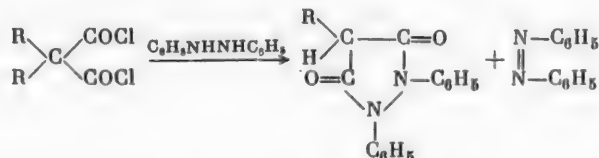
4-Bromo-1,2-diphenyl-3,5-dioxopyrazolidine (I) reacts with p-chlorophenol in the presence of metallic sodium or sodium carbonate in benzene; under these conditions a compound of the postulated structure (V) is formed.



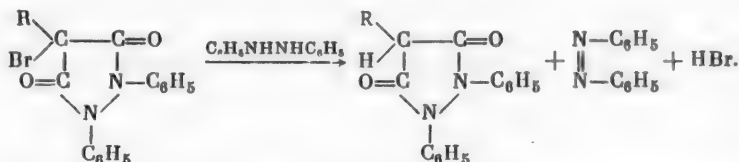
On conducting this reaction in the presence of pyridine another substance is also obtained, containing no halogen, of the composition $C_{20}H_{16}O_2N_2$ to which structure (VI) can be ascribed hypothetically.

Compound (VI) is formed when p-chlorophenol in this reaction is substituted by 2,2'-dihydroxy-5,5'-dichlorodiphenyl sulfide (IV) and also by the interaction of (I) with pyridine alone.

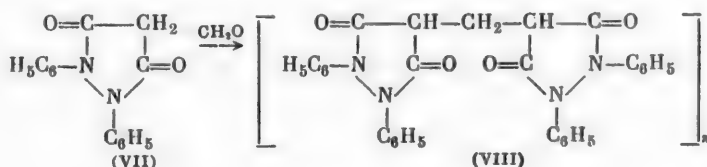
The presence of the double bond in compound (V) is indicated by the fact that it is not soluble in alkalis (i.e., it does not form an enol) and that it decolorizes bromine and potassium permanganate solutions. We suggest that these "anomalies" are very similar to the results, recently reported in the literature [2], of a study of the reaction between bromomalonyl chloride and excess hydrazobenzene. In this case 4-bromo-1,2-diphenyl-3,5-dioxypyrazolidine is not formed, but 1,2-diphenyl-3,5-dioxypyrazolidine and azobenzene are formed.



The high lability of the bromine in the pyrazolidine ring leads to the fact that in the presence of hydrazobenzene, which possesses reducing properties, the bromine is split off and the hydrazobenzene is oxidized.



However, in the reactions that we carried out the bromine is not substituted by hydrogen but by a pyrazolidine ring, which can be explained by the strong tendency of the pyrazolidine radical to self-condensation when hydrogen is present on C_4 . We also found this tendency to self-condensation in the reaction between 1,2-diphenyl-3,5-dioxypyrazolidine (VII) and formaldehyde; in this case methylene-bis-(2,3-diphenyl-3,5-dioxypyrazolidine), which we prepared by reacting methylene bismalonate ester with hydrazobenzene, is not formed, but a compound of the same composition, having different properties, possibly a polymer of the suggested formula (VIII) is formed.



EXPERIMENTAL

Investigation of the reaction between 4-bromo-1,2-diphenyl-3,5-dioxypyrazolidine and potassium thiocyanate. 3 g of 4-bromo-1,2-diphenyl-3,5-dioxypyrazolidine was added to a solution of 0.7 g of potassium thiocyanate in 15 ml of absolute alcohol at 30-40° with continuous stirring and the reaction mixture was heated in a flask under reflux on a boiling water bath, whereupon a precipitate appeared immediately. After heating for 4 hours and subsequent cooling, the precipitate was separated, washed with water, extracted with alcohol and recrystallized from chloroform. 1.8 g of material of m.p. 240-242° was obtained, consisting of white, small, needle-shaped crystals turning pink in the air and corresponding in melting point and other properties to 4,4'-bis-(1,2-diphenyl-3,5-dioxypyrazolidine) (II), which we prepared by condensing bismalonate ester with hydrazobenzene. A mixed melting point with the authentic sample showed no depression.

Found %: C 71.50, 71.89; H 4.40, 4.57; N 11.37, 11.32. $C_{30}H_{22}O_4N_4$. Calculated %: C 71.71; H 4.38; N 11.16.

Investigation of the reaction between 4-bromo-1,2-diphenyl-3,5-dioxypyrazolidine and pyridine. 2.9 g of 4-bromo-1,2-diphenyl-3,5-dioxypyrazolidine was heated with 15 ml of pyridine for 4 hours on a boiling water bath with continuous stirring. After 12 hours the precipitate that separated was filtered off and recrystallized from pyridine; 2.3 g (80%) of a compound of m.p. 253.5-254.5° was obtained. It consisted of white or yellowish crystals, insoluble in water and alkalis, of low solubility in ether and soluble in pyridine, alcohol, chloroform and acids.*

Found %: C 75.36, 75.45; H 4.56, 4.53; N 12.90, 12.85. $C_{20}H_{15}O_2N_2$. Calculated %: C 75.38; H 4.56; N 12.61.

Investigation of the reaction between 4-bromo-1,2-diphenyl-3,5-dioxypyrazolidine with p-chlorophenol. A solution of 1.6 g of p-chlorophenol in 20 ml of dry benzene and 0.29 g of metallic sodium was heated in a flask under reflux until the sodium had dissolved, 2.9 g of 4-bromo-1,2-diphenyl-3,5-dioxypyrazolidine was then added to the reaction mixture (containing a precipitate), and the mixture was refluxed for 8 hours. After filtration and removal of the benzene by vacuum distillation the residue was recrystallized from alcohol. 1.3 g (60%) of product was obtained, that did not melt up to 300°, was insoluble in alkalis and decolorized bromine and potassium permanganate solutions.

Found %: C 72.00, 72.33; H 4.34, 4.01; N 11.18, 10.87. $C_{30}H_{20}O_4N_4$. Calculated %: C 72.00; H 4.00; N 11.87.

4,4'-Methylene-bis-(1,2-diphenyl-3,5-dioxypyrazolidine). 10 g of methylene bismalonic ester [3] and 11 g of hydrazobenzene were added to 1.6 g of metallic sodium in 50 ml of absolute alcohol. After heating on an oil bath at 120-130° the alcohol was distilled off and the reaction mixture was heated for 12 hours at 180-200° with continuous stirring. After adding 200 ml of water to the cooled mixture and filtering, the precipitate that separated on acidification with hydrochloric acid was recrystallized from alcohol; 12 g (77%) of product of m.p. 210-212° was obtained. It consisted of yellowish crystals, soluble in alkalis, alcohol, ether and chloroform, and insoluble in water and acids.

Found %: C 71.87, 72.17; H 4.41, 4.51; N 10.80, 10.56. $C_{31}H_{24}O_4N_4$. Calculated %: C 72.09; H 4.65; N 10.85.

Investigation of the reaction between 1,2-diphenyl-3,5-dioxypyrazolidine and formaldehyde. 0.5 ml of 40% formaldehyde solution was added to 3.4 g of 1,2-diphenyl-3,5-dioxypyrazolidine and the mixture was heated for 3 hours on a boiling water bath, with continuous stirring. The white precipitate formed was filtered off, washed with alcohol and extracted by heating with dichloroethane, from which it separated on cooling; 2.8 g of product, m.p. 246-248°, was obtained.

Found %: C 72.49, 72.47; H 5.30, 5.07; N 10.77, 10.27. $(C_{31}H_{24}O_4N_4)_n$. Calculated %: C 70.09; H 4.65; N 10.85.

SUMMARY

1. A number of "anomalous" reactions involving 4-bromo-1,2-diphenyl-3,5-dioxypyrazolidine has been examined, in particular its reactions with potassium thiocyanate, pyridine, p-chlorophenol, etc.; the products formed did not contain sulfur or halogen.

2. It is shown that methylene-bis-1,2-diphenyl-3,5-dioxypyrazolidine is formed by reacting methylene bismalonic ester with hydrazobenzene.

LITERATURE CITED

- [1] V. G. Pesin, A. M. Khaletskii and Teng Jun-hsiang, J. Gen. Chem. 28, 3030 (1958).*
- [2] S. L. Mukherjee, P. R. Gupta, S. L. Laskar and S. Raymahasay, J. Indian Chem. Soc. 30, 841 (1953).
- [3] Ten Jun-hsiang, Dissertation, Leningrad Chemicopharmaceutical Institute (1957) [In Russian].

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* Similar results were obtained when the reaction was carried out with either p-chlorophenol or 2,2'-dihydroxy-5,5'-dichlorodiphenylsulfide.

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SYNTHESIS AND STUDY OF THE POLYMERIZABILITY OF HALOGEN-SUBSTITUTED STYRENE DERIVATIVES

VII. TRICHLOROSTYRENE AND PENTACHLOROSTYRENE

N. A. Glukhov, M. M. Koton and Z. A. Koroleva

Up to the present time information on the synthesis of trichlorostyrenes is limited to a few patents [1] which claim their practical value in dielectrics and in the synthesis of Buna-S [2]. Pentachlorostyrene has also been little studied [3]. Conditions for the synthesis of the various trichlorostyrene isomers have not been studied nor

has the effect of the structure of polyhalogenostyrene monomers on polymerizability and the properties of the polymers obtained. There is only one paper by Alfrey [4], where it is stated that in pentachlorostyrene, as a result of the presence of two chlorine atoms in the positions ortho to the vinyl group, retardation of the polymerization rate is observed.

With the object of filling this gap and continuing the systematic investigations in the field of substituted styrene we have developed syntheses of 2,4,5- and 2,3,4-trichlorostyrenes, which are not previously reported in the literature; found improved conditions for the preparation of pentachlorostyrene and studied their polymerization. Polymerization of the polyhalogenostyrenes was carried out by bulk polymerization using the dilatometric method. The ampoules, after charging with the monomers, were evacuated to $2 \cdot 10^{-1}$ mm for 2 hours and were then heated in an oil thermostat (accuracy, $\pm 0.5^\circ$). The polymer yield was determined by precipitating with methanol from benzene solution or by the bromination method; both methods were completely satisfactory with respect to accuracy of results.

The polymerization of 2,4,5-trichlorostyrene was studied at 45, 60 and 75° (Fig. 1), the polymerization of 2,3,4-trichlorostyrene — at 125 and 150° (Fig. 2) and the polymerization of pentachlorostyrene — at 125, 140 and 150° (Fig. 3).

From Fig. 1 it is seen that 2,4,5-trichlorostyrene polymerizes very readily, polymerization begins at 45°; at 75° in 2 hours, 29.5%, and in 3 hours, 43.3% conversion of monomer to

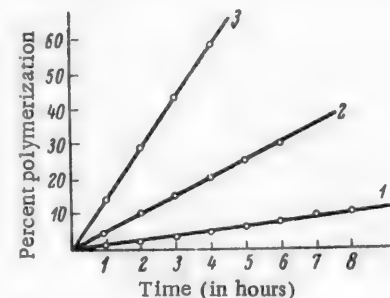


Fig. 1. Polymerization of 2,4,5-trichlorostyrene at 45° (1), 60° (2) and 75° (3).

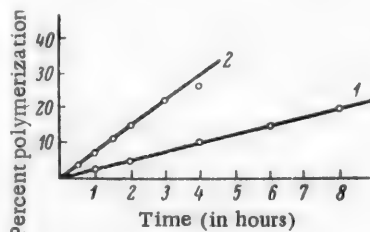


Fig. 2. Polymerization of 2,3,4-trichlorostyrene at 125° (1) and 150° (2).

polymer is reached. The isomeric 2,3,4-trichlorostyrene polymerizes with considerably more difficulty, giving at 125° in 2 hours about 5% of polymer and at 150°, in the same time, 15% of polymer. The polymerization of pentachlorostyrene (Fig. 3) proceeds slowly, forming 12% of polymer at 125° in two hours and 47% of polymer at 140°, in the same time. Comparison of the polymerization rates of polyhalogen-substituted styrene monomers with that of unsubstituted styrene (Figs. 4 and 5) shows that, with the exception of 2,4,5-trichlorostyrene, they polymerize considerably more slowly than styrene. The polymerization rates were in the following order: 2,4,5-trichlorostyrene > styrene > pentachlorostyrene > 2,3,4-trichlorostyrene.

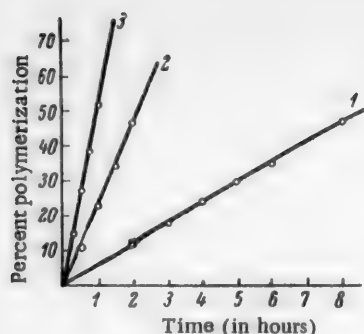


Fig. 3. Polymerization of pentachlorostyrene at 125° (1), 140° (2) and 150° (3).

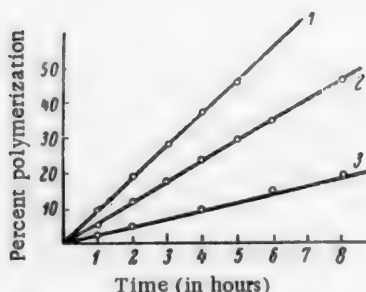


Fig. 4. Polymerization at 125° of styrene (1), pentachlorostyrene (2) and 2,3,4-trichlorostyrene (3).

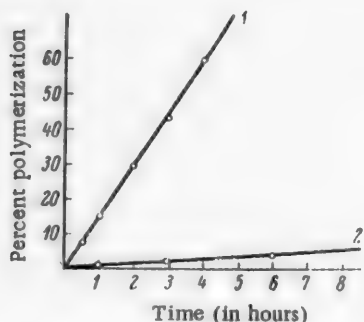


Fig. 5. Polymerization at 75° of 2,4,5-trichlorostyrene (1) and styrene (2).

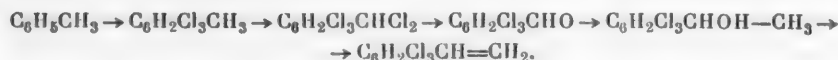
In comparing the polymerization rates of the various halogen-substituted styrenes, the effect on polymerizability of the positions of the halogen atoms in the benzene ring of the substituted styrene should be noted. As has already been reported [5], the presence of a chlorine atom in the position ortho to the vinyl group in a chlorostyrene molecule considerably increases the polymerization rate in comparison with the para isomer. It was shown further [6] that with two chlorine atoms in the benzene ring of a dichlorostyrene the 2,5 position is the most advantageous for polymerization, the formation of a high-molecular polymer, with a high polymerization rate being observed. On passing to trichlorostyrene the still-greater effect of isomerism with respect to the positions of the three chlorine atoms in the monomer molecules should be noted. In this case the 2,4,5 position is the most advantageous. The presence of five chlorine atoms in the pentachlorostyrene ring, which add weight to the monomer molecule, and the presence of two chlorine atoms in the positions (2 and 6) ortho to the vinyl group cause considerable steric hindrance to the polymerization process and pentachlorostyrene polymerizes at little more than half the rate of unsubstituted styrene. Thus in examining the effect of the structure of chloro-substituted styrene monomers on polymerization rate, the increasing effect of isomerism of styrene substituted in the benzene ring, with increasing number of nuclear substituents should be noted. In the case of the trichlorostyrenes the effect of isomerism is manifested more strongly than in the monochlorostyrenes. With respect to polymerization rate all the chlorostyrenes studied form the series:

2,4,5-trichlorostyrene > 2,5-dichlorostyrene > 2,4-dichlorostyrene > 3,4-dichlorostyrene > 4-chlorostyrene > styrene > 1,2,3,4,5-pentachlorostyrene > 2,3,4-trichlorostyrene.

Pentachlorostyrene was also bulk-polymerized in the presence of 0.1% of benzoyl peroxide at 125°; after heating for 3 hours the degree of conversion was 81% and the average molecular weight of the polymer, calculated from the relative viscosity and Billmeyer's function [7], was 28,500. The polymers of pentachlorostyrene and the trichlorostyrene isomers are transparent, brittle, thermoplastic masses, soluble in aromatic and halogenated hydrocarbons. The trichlorostyrene polymers have considerably higher softening points than that of poly-pentachlorostyrene. Copolymers of pentachlorostyrene with styrene and with methyl methacrylate, in the ratio 1:1, are transparent, colorless, thermoplastic masses.

EXPERIMENTAL

The synthesis of 2,4,5-trichlorostyrene was carried out according to the scheme



Toluene was chlorinated in the nucleus with sulfuryl chloride in the presence of anhydrous aluminum chloride and sulfur polychloride according to Silberrad [8].

1680 g of sulfuryl chloride and 168 g of sulfur polychloride were added, over a period of 3 hours, to 368 g of toluene and 40 g of anhydrous aluminum chloride at 70°. The reaction mixture obtained was washed with hot water and distilled at ordinary pressure. The fraction boiling between 220 and 245°, which consisted of almost equal parts of 2,4,5- and 2,3,4-trichlorotoluene, was collected.

Yield 72%. 2,4,5-Trichlorotoluene of m.p. 82-83° (82.4° [8]) was isolated by fractional crystallization. 2,3,4-Trichlorotoluene of m.p. 40.5° (41° [8]) was isolated from the residual waxy mass.

An 87% yield of 2,4,5-trichlorobenzalchloride in the form of a colorless liquid of b.p. 275-280° (759 mm) was obtained from 200 g of 2,4,5-trichlorotoluene by chlorination with dry, gaseous chlorine at 215-225° under illumination by an electric lamp (500 w). After repeated redistillation the 2,4,5-trichlorobenzalchloride had the following characteristics. b.p. 153-155° (15 mm), d_4^{20} 1.5956, n_D^{20} 1.5992.

105 g of 2,4,5-trichlorobenzalchloride and 500 g of oleum containing 20% sulfur trioxide were placed in a round-bottomed flask fitted with a stirrer. The mixture was stirred for 30 minutes at room temperature and then poured on to ice. After washing with sodium carbonate solution and water, crystals of 2,4,5-trichlorobenzaldehyde were steam-distilled out.

The yield of pure 2,4,5-trichlorobenzaldehyde was 70%, m.p. 111-113° (112-113° [9]).

Dinitrophenylhydrazone-yellow crystals of m.p. 249.5-250°. Found %: N 14.33, 14.35. $C_{13}H_7O_4N_4Cl_3$. Calculated %: N 14.38.

Trichlorophenylmethylcarbinol was prepared by the Grignard reaction from 2,4,5-trichlorobenzaldehyde and methylmagnesiumbromide. A methylmagnesiumbromide solution was added dropwise to a suspension of 20.95 g of the aldehyde in ether. The reaction mixture was decomposed with ice and ammonium chloride solution. Yield of unrecrystallized carbinol, 95-100%. The carbinol was redistilled and the 130-135° (0.2-0.5 mm) fraction, which solidified in the receiver as a colorless, crystalline mass of m.p. 85-86°, was collected.

Found %: Cl 47.10, 47.30; OH 7.50, 7.53. $C_8H_6Cl_3OH$. Calculated %: Cl 47.23; OH 7.54.

The carbinol obtained was dehydrated in toluene solution over activated aluminum oxide at 350° and a residual pressure of 115 mm. The receiver was cooled in liquid nitrogen. The condensate obtained was washed with 10% sodium hydroxide solution and with saturated calcium chloride solution. The liquid was dried, the toluene removed and the residue distilled in vacuo. 2,4,5-Trichlorostyrene, a crystalline, colorless material, when distilled in vacuo at 90° (0.04 mm).

B.p. 35°, n_D^{36} 1.5923, d_4^{36} 1.3910, MR_D 50.45; calc. 49.72. Monomer content 99.5% (determined by bromination method).

The synthesis of 2,3,4-trichlorostyrene was similar to that of 2,4,5-trichlorostyrene. A 90% yield of 2,3,4-trichlorobenzalchloride was obtained from 2,3,4-trichlorotoluene by chlorination in the side-chain, and consisted of colorless crystals of m.p. 82-83° (from petroleum ether) (84° [9]). 2,3,4-Trichlorobenzaldehyde, m.p. 85.5-86° (86° [10]) was obtained in 90% yield by hydrolysis of the benzalchloride.

The 2,4-dinitrophenylhydrazone of the aldehyde had m.p. 263.5-237.5°.

2,3,4-Trichlorophenylmethylcarbinol was prepared in the usual way, by condensation of the aldehyde with methylmagnesiumbromide and decomposition of the complex formed, with water. Yield after two redistillations in vacuo at 123-125° (0.5-0.8 mm), 80%. The alcohol was a very viscous, colorless liquid.

B.p. 123-125° (0.5-0.8 mm), d_4^{20} 1.4696, n_D^{20} 1.5854.

Found %: Cl 46.95, 47.15; OH 7.48, 7.46. $C_8H_6Cl_3OH$. Calculated %: Cl 47.23; OH 7.54.

The alcohol was dehydrated as in the case of 2,4,5-trichlorophenylmethyl carbinol. A transparent, colorless, liquid was obtained, that solidified to a crystalline mass on cooling to -5°.

B.p. 80-81° (0.02 mm), n_D^{20} 1.5932, d_4^{20} 1.4020.

Found %: Cl 51.26, 51.30. $C_6H_2Cl_3CH=CH_2$. Calculated %: Cl 51.4. Monomer content 99.7% (determined by bromination method).

Synthesis of pentachlorostyrene. From the chlorination of toluene (184 g) with sulfuryl chloride (1485 g) in the presence of 1% of sulfur polychloride and anhydrous aluminum chloride, pentachlorotoluene was obtained in 89% yield after one recrystallization from benzene; m.p. 217.5-218° (218° [8]). The pentachlorotoluene ob-

tained was converted to pentachlorobenzalchloride by chlorination at 220-225° with a current of dry chlorine and illumination of the reaction flask by an electric lamp (500 w). Yield after redistillation in vacuo, 85%, m.p. 118-119° (119.5 [11]).

Pentachlorobenzaldehyde was prepared by Newton's method as described by Ross [3]. Yield of crude product, 90-95%. After two recrystallizations from acetone the yield was 75-80% and the product had m.p. 198-198.5° (197-199° [3]).

Preparation of the carbinol from the aldehyde was carried out according to Lock [11], with some modifications. Instead of methyl iodide, methyl bromide was used in order to prevent dehydration of the carbinol during the course of the reaction, which can occur in the presence of traces of iodine. 14 g of fine-crystalline pentachlorobenzaldehyde was suspended in 120 ml of ether in a two-necked, round-bottomed flask and a filtered solution of Grignard reagent, prepared from 1.5 g of magnesium, 6.4 g of methyl bromide and 70 ml of ether, was added gradually. The mixture was heated for 4 hours, allowed to stand overnight and decomposed with saturated ammonium chloride solution; ether was added to the mixture, the ethereal layer was separated, washed, dried over calcium chloride and the solvent was distilled off. The residue was recrystallized from dilute alcohol yielding 7 g of methylpentachlorophenylcarbinol (47%) of m.p. 126° (126° [11]).

The carbinol obtained was dehydrated over activated aluminum at 310 ± 5° and 15-20 mm. The pentachlorostyrene was passed over aluminum oxide a second time in order to remove traces of the alcohol and the product was recrystallized from ethanol. The yield after passing twice over activated aluminum oxide and recrystallizing twice, was 42%. Pentachlorostyrene — long, thin needles of m.p. 113.5-114° (113.5-114.5° [3]).

SUMMARY

1. 2,3,4- and 2,4,5-trichlorophenylmethyl carbinol, and 2,3,4- and 2,4,5-trichlorostyrene have been synthesized and characterized for the first time. Improvements have been made in the conditions for the preparation of pentachlorostyrene of a high degree of purity.

2. The polymerization of tri- and pentachlorostyrenes has been studied over the temperature range from 45 to 150°.

3. It is shown that with respect to polymerization rate the polyhalogenostyrenes studied form the series: 2,4,5-trichlorostyrene > 1,2,3,4,5-pentachlorostyrene > 2,3,4-trichlorostyrene.

4. It has been found that the effect of isomerism of the substituents in the benzene ring on polymerization rate, increases with increasing numbers of chlorine atoms.

LITERATURE CITED

- [1] U.S. Patent 2,463,897; Chem. Abs. 43, 4514 (1949).
- [2] C. Marvel, Ind. Eng. Chem. 39, 1486 (1947).
- [3] U.S. Patent 2,290,758, 2,290,759; Chem. Abs. 37 (1943); S. Ross, M. Markarian and M. Nazzewski, J. Am. Chem. Soc. 69, 1914 (1947).
- [4] T. Alfrey, J. Am. Chem. Soc. 71, 3235 (1949).
- [5] M. M. Koton, E. M. Moskvina and F. S. Florinskii, J. Gen. Chem. 20, 1843 (1950).*
- [6] M. M. Koton, E. M. Moskvina and F. S. Florinskii, J. Gen. Chem. 22, 769 (1952).*
- [7] F. Billmeyer, J. Pol. Sci. 4, 83 (1949).
- [8] O. Silberrad, J. Chem. Soc. 127, 2677 (1925).
- [9] E. Seelig, Lieb. Ann. 237, 147 (1886).
- [10] H. C. Brimelow, R. L. Jones and T. P. Metcalfe, J. Am. Chem. Soc. 73, 1208 (1951).
- [11] G. Lock, Ber. 72B, 300 (1939).

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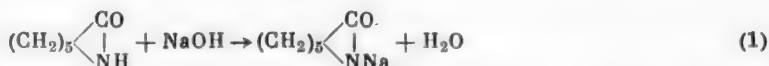
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ON THE PROCESS OF FORMATION OF POLYAMIDE RESINS

VIII. THE QUESTION OF THE ALKALINE POLYMERIZATION OF ϵ -CAPROLACTAM

A. S. Shpital'nyi and N. S. Iablochnik

It has been found in work on the conversion of caprolactam to polymer in the presence of alkaline activators [1-4] that many reagents possess alkaline properties capable of activating the process of formation of polyamide macromolecules. In discussions on the nature of this process it has been noted that in its initial stages, as a result of interaction of the activator and the lactam, the alkaline salt of the lactam is formed, which is the real initiator that brings about the rapid course of the reaction in question. Indications of the formation of such salts can be found not only in the processes described where the activators are one or another of the alkali metals [2], but also in work on the polymerization of caprolactam with the help of alkaline agents such as sodium hydroxide, alkali metal acetates, etc. [3,4]. In the latter case some authors put forward the following scheme for the formation of the salt [3]



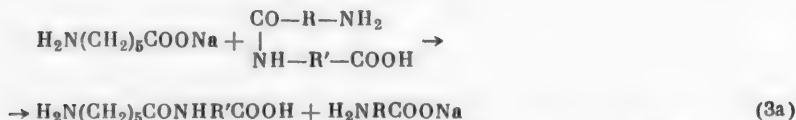
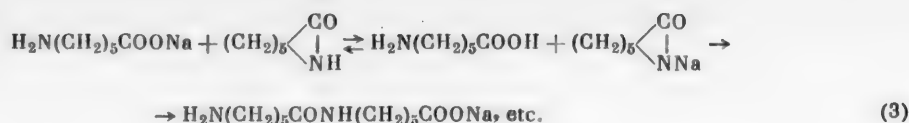
and others limit themselves to an account of the way in which it takes part in polymer formation [4]. It has thus been assumed that in alkaline polymerization all the alkaline activators give rise to the formation of the alkali salt of the lactam, although indications of the possibility of such a transformation are cited only for the case where the activator is an alkali metal [2].

Our work shows that the reaction of caprolactam with alkali at a temperature of about 270° does not result in the formation of the alkali salt of the lactam but of the salt of aminocaproic acid. This follows from experiments on the reaction between alkali and caprolactam, with a considerable excess of alkali. It was considered that excess alkali would create conditions that would exclude the possibility of polymer formation and that would enable easily analyzable, low-molecular compounds to be obtained as end products. If the reaction mass should contain the alkali salt of the lactam in accordance with Eq. (1) it should be possible to extract the lactam unchanged after neutralization. In fact, in the reaction with sodium hydroxide either the salt of ϵ -aminocaproic acid or polymer was extracted from the reaction mass, depending on the conditions.

The formation of ϵ -aminocaproic acid in the reaction between sodium hydroxide and caprolactam is explained by reaction (2)



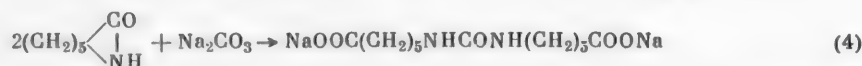
It is quite possible that the compound $\text{HOOC}(\text{CH}_2)_5\text{NHNa}$ is formed as an intermediate product and that because of its instability it immediately rearranges to the Na-salt of ϵ -aminocaproic acid. It was found in subsequent experiments that this salt is also capable of initiating the conversion of caprolactam to polymer. It should not be concluded from this that the caprolactam salt, and particularly its anion, does not take part in the process, because it would then be difficult to explain the rapid course of alkaline polymerization. Hence, if the experimental facts are taken into account in the polymer formation scheme and at the same time participation of the lactam salt is not excluded, the scheme can be depicted in the following form:



Reaction (3a) which brings about depolymerization or transamidation of the polymer [5] differs from the corresponding reaction of Griel [3] in that it is the aminocaproic salt (or its derivatives) and not the caprolactam salt (or its derivatives) that takes part.

Reactions (2), (3) and (3a) find confirmation in the conversion of the polyamide polymer to caprolactam by the action of sodium hydroxide at 270-300°, which is used as one of the methods of regeneration of the lactam from the waste products of the polyamide production [6].

If sodium carbonate reacts with caprolactam similarly to NaOH then the formation of the polymerization initiator when sodium carbonate takes part in the reaction can be depicted by the following scheme.



However, we have not yet succeeded in isolating the latter compound. It has already been stated above that by the action of an excess of even sodium carbonate on caprolactam, low-molecular compounds are not isolated from the reaction mass, but a water-insoluble polymer is isolated. The formation of a macromolecular compound is caused evidently by the low solubility of sodium carbonate in the caprolactam melt [3].

EXPERIMENTAL

Reaction of caprolactam with NaOH. A mixture of 2 g of powdered caprolactam and 1.2 g of powdered NaOH was heated in vacuo at 3 mm in an ampoule in a water bath for a few hours, to remove traces of moisture. The ampoule was then sealed and maintained at 280° for 2 hours. The melt was dissolved in water and the solution neutralized with 0.5 N sulfuric acid solution, after which it was evaporated on the water bath. The dry residue was treated with ether. No caprolactam was detected in the ethereal extract. The residue was treated with methyl alcohol. Precipitation of the alcohol solution with ether yielded a crystalline material which after recrystallization from methyl alcohol had m.p. 202°. A mixture with ϵ -aminocaproic acid melted without depression. Yield of ϵ -aminocaproic acid, 75.75%.

Reaction of the Na-salt of ϵ -aminocaproic acid with caprolactam. The Na-salt of ϵ -aminocaproic acid was prepared by addition of the calculated quantity of a standardized sodium hydroxide solution to a solution of ϵ -aminocaproic acid, and removal of the water by evaporation of the solution on the water bath.

A mixture of 0.0962 g of this salt and 0.856 g of caprolactam was placed in an ampoule and after displacement of the air by nitrogen the ampoule was sealed and maintained at 280° for 2 hours. After working up with ether and boiling with water for 15 minutes, the yield of resin was 80%. A molecular weight of 7,000 was found by titration of the resin in benzyl alcohol solution [7].

Reaction of caprolactam with sodium carbonate. A mixture of 3 g of powdered caprolactam and 3 g of powdered, anhydrous sodium carbonate was heated for 2 hours at 280° in a sealed ampoule. On treating the resulting melt with hot water for $\frac{1}{2}$ hour, the major portion did not dissolve. The residue was filtered off and washed with water to neutral reaction. Yield of resin 65%. Molecular weight found, 1,035.

After neutralizing with sulfuric acid, the combined filtrate and water washings were evaporated on the water-bath. The dry residue was treated with ether. The residue after removal of ether from the extract consisted of a crystalline material that gave no melting point depression with caprolactam. The quantity of caprolactam extracted was 13.33%.

SUMMARY

1. It has been found that by the reaction of caprolactam with excess NaOH at 280° the alkali salt of ϵ -aminocaproic acid is formed.
2. A scheme is put forward for the reaction process between caprolactam and sodium hydroxide and for the conversion of caprolactam to polymer with the help of the alkali salt of ϵ -aminocaproic acid.

LITERATURE CITED

- [1] Swedish Patent 99,037; Centralblatt. 1940, II, 2982; U.S. Patent 2,251,519.
- [2] W. E. Hanford and R. M. Joyce, J. Polymer Sci. 3, 167 (1948).
- [3] W. Griel, Stenogram of communication on scientific-technical collaboration of the USSR and national-democratic countries in the field of production of chemical fibers, State Light-Industry Press, 103 (1956);* W. Griel and H. Sieber, Faserforsch. u. Textiltechn. 6, 329 (1955); W. Griel, Faserforsch. u. Textiltechn. 6, 262 (1955); A. Gordienko, W. Griel and H. Sieber, Faserforsch. u. Textiltechn. 6, 105 (1955).
- [4] O. Wichterle, Faserforsch. u. Textiltechn. 6, 237 (1955); Stenogram of communication on scientific-technical collaboration of the USSR and national-democratic countries in the field of production of chemical fibers, State Light-Industry Press, 217 (1956). *
- [5] V. V. Korshak, Advances in Chemistry, 21, 121 (1952).
- [6] Z. A. Rogovin, Chemistry and Technology of Artificial Fibers, State Light-Industry Press, 643 (1952). *
- [7] J. E. Waltz and G. B. Taylor, Anal. Chem. 19, 448 (1947).

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N-ALKYLATED AND N-ARALKYLATED MORPHOLINE DERIVATIVES

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The use of morpholine in various branches of industry [1] has aroused interest in the study of the properties of its various derivatives, which contain the morpholine ring and which, in many cases, possess valuable properties. In recent years isolated representatives of such N-substituted morpholine derivatives in which the hydrogen of the morpholine ring nitrogen is substituted by various hydrocarbon radicals of both the aliphatic and aromatic series, have begun to find application. Compounds of this type are used at the present time for the production of surface-active and bactericidal substances [2, 3], as insecticides [4], as plant growth stimulators [5, 6], for the preparation of pharmacologically active substances [7-9], as antioxidant additives for lubricating oils [10], in the form of nitrites as inhibitors of corrosion by water and aqueous salt solutions [11], for the production of vat-dye leuco-compounds [12] and as catalysts in chemical reactions [13].

At the same time information in the literature on the preparation and properties of N-substituted derivatives of morpholine is very scanty and this considerably hinders investigation of the technical properties and further study of the possibility of using this class of compound. Examination of the individual cases of preparation of N-alkyl and N-aralkyl morpholine derivatives shows that the methods described can be divided into two groups: I) reactions in which morpholine is one of the starting materials, and II) reactions in which, in addition to condensation of the starting materials, cyclization must take place to form the morpholine ring. The reactions of morpholine with alkyl halides [7, 8, 14], or aldehydes [15, 16] and organomagnesium synthesis (through the intermediate formation of 4-morpholinomethylethyl ether) [17] belong to the first group. The following reactions belong to the second group: the reaction of primary amines with ethylene chlorohydrin [9], with dihalo-substituted ethyl ether (β, β' -diodoethyl ether [18, 19] or β, β' -dichloroethyl ether [20]) or with compounds of the type $\text{RSO}_2\text{O}(\text{CH}_2)_n\text{OSO}_2\text{R}$ [21] and vapor-phase dehydration of N,N-bis-(2-hydroxyethyl)-alkylamines [22].

Comparison of these methods of preparation shows that with morpholine present the first group of reactions is the most practicable. However, data on the yields of the morpholine derivatives are almost absent from the literature.

In the present work N-substituted morpholine derivatives were prepared by the reaction between morpholine and the respective alkyl or aralkyl halides for the purpose of studying their action on lubricating oils. The data in the literature on carrying out this reaction are very incomplete and data on the yields of the alkylated products are completely absent. Hence, in the process of conducting this work we selected the optimal conditions for preparing butylmorpholine; the other morpholine derivatives were then prepared in an analogous manner.

We synthesized the following morpholine derivatives under the conditions described below: ethyl-(II), propyl-(III), n-butyl-(IV), n-hexyl-(V), sec -n-octyl-(VI), n-octadecyl-(VII), benzyl-(VIII), α -naphthylmethyl morpholine (IX) and 9, 10-bis (morpholinomethyl)-anthracene (X). Compounds (VI) and (X) are not described in the literature.

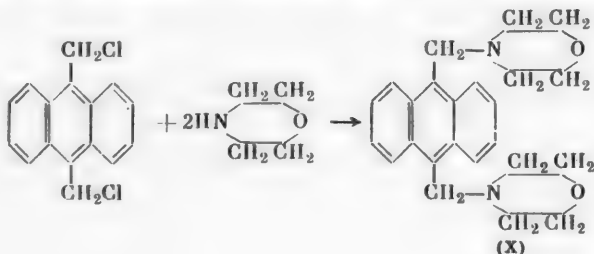
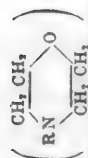


TABLE 1

Physicochemical Properties of N-Substituted Alkylated and Arylalkylated Morpholine Derivatives



No. of compound	R	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	MRD		Kinetic viscosity at 20° (in stokes)	Yield ² (in %)
					found	calculated		
(I)	H	127–128°	1.030	1.4510	23.52	23.71	0.0271*	77
(II)	C ₂ H ₅	138–139	0.915	1.4400	—	—	0.0129*	59
(III)	n-C ₄ H ₉	150–152	0.9110*	1.4471*	37.80	37.91	0.0175*	68
(IV)	n-C ₆ H ₁₃	175–177	0.9068*	1.4460*	41.95	42.52	0.0212*	75
(V)	n-C ₈ H ₁₇	215–217	0.8909*	1.4492*	52.08	51.76	0.0276*	84
(VI)	CH ₃ -(CH ₂) ₅ -CH- CH ₃	248–249*	0.8898*	1.4551*	60.63	60.99	—	76
(VII)	n-C ₁₀ H ₂₁	230–232 (10) M.P. 39	—	—	—	—	—	63
(VIII)		138–140 (6)	1.0387	1.5302	52.29	52.77	—	65
(IX)		178–180 (4)	1.1010*	1.6035*	70.71	70.80	0.3118*	49
(X)		M.P. 229–230*	—	—	—	—	(at 50°) —	46

Notes. 1) The asterisks denote data obtained by us that are not recorded in the literature. 2) Yields are calculated on the alkyl halide taken.

3) According to [22], b.p. 128–130°, d_4^{20} 0.9994, n_D^{20} 1.4545. 4) According to [19], b.p. 138–139°, d_4^{25} 0.9166, n_D^{20} 1.4400. 5) B.p. 43–46° 7 (mm) [17], 95–98° (22 mm) [16], 150° [3]. Yield from Grignard synthesis, 43.4% [17]. 6) B.p. 67–68° (10 mm) [22], 80–84° (15 mm) [16], 85–99° (25 mm) [15], 174° [4]. In [21] the m.p. of 213–214° is incorrectly quoted for butylmorpholine; its hydrochloride has this melting point. 7) B.p. 86–87° (6 mm) [17], 204° [3]. Yield according to [17], 59.7%. 8) B.p. 160–175° (0.3 mm) [20], 200° (4 mm) [3] m.p. 25° [8], 40° [3]. Yield [21] from condensation of octadecylamine with dichloroethyl ether, 88%. 9) B.p. 128–129° (13 mm) [22], 251° [7], d_4^{20} 1.0387 [19]; according to our results, n_D^{20} 1.0340, 1.5131 [9], 1.5256 [19]. Yield from synthesis by other methods, according to [17], 64.4%. 10) B.p. 185–190° (9 mm) [17]. Yield according to [14], 52%.

TABLE 2

Name of compound	pH
Morpholine	10.60
Ethylmorpholine	11.00
Propylmorpholine	9.90
Butylmorpholine	10.05

Some physicochemical constants were determined for the morpholine derivatives that we synthesized; in many instances these have not been previously recorded in the literature. Data on the properties of the N-substituted morpholine derivatives and the yields obtained in our experiments are given in Table 1. These figures give an indication of the variation in boiling point, density, refractive index and viscosity in the homologous series of N-alkylated and N-aralkylated morpholine derivatives. The pH value of a 0.1 M aqueous solution of some of the morpholine derivatives was measured with an LP5 potentiometer and a glass electrode. The results of these measurements are given in Table 2.

EXPERIMENTAL

We carried out experiments* on the preparation of butyl morpholine under various conditions: equimolar quantities of morpholine and butyl iodide or bromide were reacted together using potassium hydroxide as condensing agent and alcohol or benzene as solvent. The yield of butylmorpholine under these conditions was less than 50%. Increasing the time of heating to 10 hours did not increase the yield of reaction product. Carrying out the condensation with an excess of morpholine to combine with the hydrohalic acid (described in the case of the synthesis of α -naphthylmethylmorpholine [14]) was shown by our experiments to be very advantageous also for the preparation of the various alkylated morpholine derivatives, because the morpholine salt formed is insoluble in the majority of organic solvents, is easily separated from the main reaction product and the spent, excess morpholine can be regenerated. Carrying out the condensation without solvent enabled the reaction temperature to be increased to 130-140°, a saving to be made in the number of operations necessary and the yield of reaction product to be increased, particularly in the preparation of alkylated morpholine derivatives.

A description of the general method of preparation of N-substituted morpholine derivatives is given below. An account of the synthesis of compound (X) is also given because a different method was used for its isolation and purification.

Preparation of N-alkylated and N-aralkylated derivatives of morpholine. To morpholine (0.2 moles), prepared according to [23], placed in a round-bottomed flask fitted with a reflux condenser and dropping funnel, the alkyl halide (0.1 mole) was added gradually with external cooling and stirring, after which the reaction mixture was heated in an oil bath for 5 hours at 140°. At the end of the heating period the reaction product was extracted with ether. The solid residue, containing the morpholine halide salt, was filtered off. The ethereal extract was dried over sodium sulfate. The product obtained after removal of the ether was distilled on an oil bath (in the case of alkylated morpholine derivatives) or vacuum-distilled (in the case of aralkylated derivatives). Morpholine can be regenerated from the residual halide salt by distillation, on heating the salt with solid alkali (calculated in the proportion 0.5 g of KOH to 1 g of salt).

By this means we prepared compounds III, IV and VII-IX, in the yields indicated in Table 1.

Synthesis of 9,10-bis(morpholinomethyl)-anthracene (X). The starting material 9,10-bis(chloromethyl)-anthracene was prepared by chloromethylation of anthracene according to [24].**Purification of the crude product obtained was carried out by a method similar to that of [25] by a twofold suspension of the impure material in dioxan. The residue, insoluble in dioxan, after drying in a vacuum desiccator was recrystallized from hot toluene. The precipitate from the filtrate (hot filtration) was a light-yellow substance of m.p. 281°. The 9,10-bis(chloromethyl)-anthracene obtained was analyzed for chlorine content by oxidation with sodium peroxide and subsequent titration by the Volhard method [26].

Found %: Cl 25.50. $C_{12}H_{12}Cl_2$. Calculated %: Cl 25.60.

9,10-bis(chloromethyl)-anthracene can cause irritation of the mucous membrane of the eyes, swellings of the face and eczema-like irritation of the skin.

* With the assistance of student B. N. Klopov.

** The experiments on the chloromethylation of anthracene were carried out with the assistance of students O. A. Almazov and S. A. Tikhomirov.

2.7 g of 9,10-bis (chloromethyl)-anthracene and 8.6 g of morpholine were refluxed in an oil bath at 125-130° for 1 hour. The reaction mixture was then left to stand for 24 hours after which it was diluted with water. The precipitate that separated was filtered off and thoroughly washed with water until the aqueous washings were free from Cl^- , then dried in a drying oven (80°). 1.8 g (46.2 %) of a yellow substance of m.p. 190-200° was obtained. In another experiment the crude product melted at 213°. The yellow solid obtained was treated for purification with concentrated hydrochloric acid (about 75 ml), the hydrochloric acid solution was filtered and 9,10-bis (morpholinomethyl)-anthracene was precipitated from the filtrate by sodium hydroxide solution (added until the reaction to litmus was alkaline). The light-yellow precipitate formed was filtered off, washed with water and dried. It could be recrystallized from hot benzene. M.p. 229-230°. 9,10-bis (morpholinomethyl) anthracene is insoluble in water, alcohol and ether, difficultly soluble in acetone and soluble in benzene and glacial acetic acid.

Found %: C 76.27; H 7.59; N 7.13. $\text{C}_{22}\text{H}_{29}\text{O}_2\text{N}_2$. Calculated %: C 76.56; H 7.49; N 7.44.

SUMMARY

1. Improved conditions have been found for the preparation of N-alkylated and N-aralkylated morpholine derivatives by condensation of morpholine with alkyl and aralkyl halides. Nine morpholine derivatives have been synthesized in this way, with yields from 45 to 84%.

2. 9,10-bis (morpholinomethyl)-anthracene and sec -n-octylmorpholine, not described in the literature, have been prepared.

3. The densities, refractive indices and viscosities, not recorded in the literature, of some of the compounds prepared, have been determined.

4. Comparison of the constants obtained shows that with increasing length of the aliphatic radical substituting the hydrogen on the nitrogen atom of the morpholine ring, the boiling points of the derivatives increase, the densities decrease and the refractive indices and viscosities increase. The introduction of aromatic rings raises the boiling points, densities, refractive indices and viscosities to an increasing extent with increase in the number of rings.

LITERATURE CITED

- [1] N. N. Zimakov, *Ethylene Oxide*, 222 (1946).*
- [2] U. S. Patent 2,602,791 (1947).
- [3] U.S. Patent 2,602,791 (1952).**
- [4] A. W. A. Brown, *J. Econ. Entomol.* 42, 399 (1949).
- [5] S. Newmann, W. Tones and M. Renoll, *J. Am. Chem. Soc.* 69, 718 (1947).
- [6] R. L. Jones, J. Madinaveitia, T. P. Metcalfe and W. A. Sexton, *Biochem. J.* 47, 110 (1950).
- [7] R. Hazard, E. Corteggiani and S. H. Renard, *C. r.* 227, 95 (1948).
- [8] J. B. Niederl, H. W. Salzberg and J. J. Shatynski, *J. Am. Chem. Soc.* 70, 618 (1948).
- [9] L. P. Kyrides, F. C. Meyer, F. B. Zienty, J. Harvey and L. W. Bannister, *J. Am. Chem. Soc.* 72, 745 (1950).
- [10] U.S. Patent 2,516,654 (1950).
- [11] U.S. Patent 2,432,840 (1947).
- [12] British Patent 585,106 (1947).
- [13] R. Baltzly, *J. Am. Chem. Soc.* 74, 4586 (1952).
- [14] M. T. Leffler and E. H. Volwiller, *J. Am. Chem. Soc.* 60, 896 (1938).
- [15] U.S. Patent 2, 578,787 (1951).

*In Russian.

**As in original — Publisher's note.

- [16] P. L. deBenneville and J. H. Macartney, *J. Am. Chem. Soc.* 72, 3073 (1950).
- [17] J. P. Mason and M. Zief, *J. Am. Chem. Soc.* 62, 1450 (1940).
- [18] L. Knorr, *Lieb. Ann.* 301, 18 (1898).
- [19] H. T. Clarke, *J. Chem. Soc.* 101, 1808 (1912).
- [20] J. G. Erickson and J. S. Keps, *J. Am. Chem. Soc.* 76, 3589 (1954).
- [21] *Dictionary of Organic Compounds*, III, 537 (1953).
- [22] F. F. Blicke and Z. B. Zienty, *J. Am. Chem. Soc.* 61, 771 (1939).
- [23] M. L. Medard, *Bull. Soc. Chim.* 5 Ser. 3, 1338 (1936).
- [24] E. Iu. Gudrinletse and G. Ia. Vanag, *J. Gen. Chem.* 25, 3123 (1955). *
- [25] M. W. Miller, R. W. Amidon and P. O. Tawney, *J. Am. Chem. Soc.* 77, 2845 (1955).
- [26] R. P. Lastovskii, *Technical Analysis in the Production of Intermediate Products and Dyestuffs* 81 (1949). **

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** In Russian.

THE ENTHALPY OF FORMATION OF COMPOUNDS OF CADMIUM WITH PHOSPHORUS, ARSENIC AND ANTIMONY

S. A. Shchukarev, M. P. Morozova and M. M. Bortnikova

It was reported earlier that the variation in the heats of formation of the series of compounds of nitrogen, phosphorus, arsenic, antimony and bismuth with zinc, in contrast to that of the heats of formation of the compounds of these elements with magnesium or strontium, is subject to the rule of secondary periodicity [1]. We were interested in examining how the heats of formation of compounds of cadmium with the elements of the main subgroups of Group V behave. If cadmium in fact forms the compound CdN_2 with nitrogen, then it is extremely unstable [2]. With phosphorus it forms the compound Cd_3P_2 and also a phosphide of the probable formula CdP_2 , again evidently of poor stability [3].

In the system cadmium-arsenic the existence of the compound Cd_3As_2 has been established [3-5].

The system cadmium-antimony has been studied fairly fully by a number of authors [6-8]. In this system the existence of the compounds CdSb and Cd_3Sb_2 has been established.

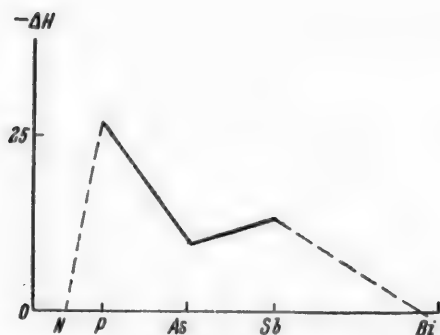
Compounds of cadmium with bismuth, at least thermodynamically stable compounds, do not exist.

For the synthesis of the compounds, metallic cadmium, purified by distillation in high vacuum, and chemically pure arsenic, antimony and phosphorus, tested by spectrographic analysis, were used.

Cadmium phosphide Cd_3P_2 was prepared by the action of phosphorus on metallic cadmium at 450-500°. The two materials were placed separately in boats in a Pyrex glass tube, which was sealed after thorough evacuation. Excess phosphorus was taken with respect to its content in Cd_3P_2 . At the end of the reaction between the cadmium and phosphorus the excess of the latter was distilled off. Cadmium phosphide prepared in this way is a dark-gray crystalline powder. The x-ray spectrograms showed no lines corresponding to the free components.

Cadmium arsenide Cd_3As_2 was prepared in the same way as for cadmium phosphide but at a higher temperature (600-700°). X-ray spectrograms recorded for the preparations obtained in this way did not show lines corresponding to the free components.

Variation of enthalpy of formation of compounds of cadmium with the elements of the main subgroup of Group V, with atomic number.



We prepared cadmium antimonide by fusing the components together in the stoichiometric ratio. The fusion was carried out in sealed Pyrex glass ampoules at 550-560° for 8-10 hours.

The x-ray spectrogram of the preparation showed a single structure for this material also. The results of analysis of the materials synthesized are given below.

Found % Cd 84.63, 84.35; P 15.35, 15.43. Cd_3P_2 . Calculated % Cd 84.47; P 15.53.
Found % Cd 69.45, 69.30; As 30.55, 30.64. Cd_3As_2 . Calculated % Cd 69.20; As 30.80.
Found % Cd 58.10, 57.85; Sb 41.87, 41.75. Cd_3Sb_2 . Calculated % Cd 58.06; Sb 41.94.

TABLE 1

Enthalpy of Formation (in kcal/g mole)

$3\text{Cd}_\text{P} + 2\text{P} = \text{Cd}_3\text{P}_2$	$3\text{Cd}_\text{P} + 2\text{As} = \text{Cd}_3\text{As}_2$	$3\text{Cd}_\text{P} + 2\text{Sb} = \text{Cd}_3\text{Sb}_2$
-29.5	-11.5	-15.4
-25.4	- 8.9	-13.3
	- 9.5	-12.1
Mean $\dots -27.4 \pm 2.0$	-10.0 ± 2.0	-13.9 ± 1.8

TABLE 2

Compound	Heat of formation (kcal)	Compound	Heat of formation (kcal)
ZnO	83.40	CdO	62.4
ZnS	44.3	CdS	34.5
ZnCl ₂	99.3	CdCl ₂	93.1
ZnSe	34.0	CdSe	25.0
ZnTe	28.2	CdTe	24.5
Zn ₃ P ₂ ^[12]	98.0	Cd ₃ P ₂	27.4
Zn ₃ As ₂ ^[13]	30.5	Cd ₃ As ₂	10.0
Zn ₃ Sb ₂ ^[14]	48.0	Cd ₃ Sb ₂	13.9

In order to determine the enthalpy of formation of cadmium phosphide, arsenide and antimonide use was made of their reaction with 1 N potassium bromide saturated with bromine, the latter being present in excess.

As we did not know exactly the reaction products of the compounds being investigated and KBr solution saturated with bromine, we determined the heats of reaction of the corresponding elements under the same experimental conditions as for the compounds. For the heat of reaction of cadmium the figure 87.6 ± 1 was obtained, for arsenic 103 ± 1.0 and for phosphorus 173.6 ± 2.0 kcal/g atom.

The calorimetric method has been described previously [9]. The "water-equivalent" of the calorimeter was determined from the heat of reaction of antimony with hydrochloric acid solution (1:4) saturated with bromine, the standard value of the heat of reaction of antimony under these conditions being taken as 91.6 kcal/g atom.

The reaction of cadmium phosphide and arsenide with $\text{KBr}-\text{Br}_2$ solution resulted in complete solution of the materials; in the case of cadmium antimonide the cadmium went into solution during the course of the calorimetric experiment and the antimony remained in the form of the element.

The enthalpy of formation of the compounds of cadmium with the elements of the main subgroup of Group V was obtained as the difference between the heats of reaction of the elements (that went into solution) with $\text{KBr}-\text{Br}_2$ solution and the heats of reaction of the compounds with the same solution.

By this means the respective values of the enthalpy of formation (in kcal per gram mole) of the compounds of cadmium with phosphorus, arsenic and antimony, given in Table 1, were found.

The value found by us for Cd_3As_2 is close to that found by Weibke and Kubaschewski [10] (-14.0 ± 2.5 kcal/g mole). The enthalpy of formation of Cd_3Sb_2 was determined by Bietz and Haase [11]: their figure was 4 kcal/g mole. Our figure seems the more probable, being in good agreement with the high stability of this compound.

From the graph, which shows the variation in enthalpy of formation of compounds of cadmium with the elements of the main subgroup of Group V as a function of the atomic numbers of the latter, it is obvious that the variation in enthalpy of formation in the series $\text{Cd}_3\text{N}_2-\text{Cd}_3\text{Bi}$ is subject to the rule of secondary periodicity.

As a rule the heats of formation of zinc compounds exceed those of the analogous cadmium compounds by not more than 35%. The compounds with the elements of the main subgroup of Group V form an exception (Table 2).

The change from zinc to cadmium is accompanied in this case by a sharp reduction (approximately 3-fold) in the heats of formation. This interesting phenomenon is in full accord with the fact that by a further change to mercury — the last element of the secondary subgroup of Group II — further reduction in these values evidently takes place because compounds of mercury with phosphorus, arsenic and antimony cannot generally be prepared.

SUMMARY

1. The values of the enthalpy of formation of Cd_3P_2 , Cd_3As_2 and Cd_3Sb_2 have been determined.
2. It is stated that against the background of the general closeness of the values of the heats of formation of analogous zinc and cadmium compounds there is a marked difference in the heats of formation of their compounds with the elements of the main subgroup of Group V. The substitution of zinc by cadmium in these compounds is accompanied by a sharp reduction in the heats of formation.
3. The variation in the heats of formation of compounds of cadmium with the elements of the main subgroup of Group V are subject to the rule of secondary periodicity.

LITERATURE CITED

- [1] S. M. Ariia, M. P. Morozova and S. A. Shchukarev, *J. Gen. Chem.* 27, 1131 (1957).*
- [2] H. Hahn and R. Jusa, *Z. anorg. Ch.* 244, 111 (1910).
- [3] M. V. Stackelberg and R. Paulus, *Z. Phys. Ch.* (3) 28, 427 (1935).
- [4] A. Granger, *C. r.* 138, 574 (1904).
- [5] S. F. Zemezuzny, *Metallographie*, 4, 228 (1913).
- [6] W. Treitschke, *Z. anorg. allg. Ch.* 50, 217 (1906).
- [7] N. S. Kurnakow and N. S. Konstantinow, *Z. anorg. allg. Ch.* 58, 12 (1908).
- [8] F. Hall, H. Nowotny and H. Tompe, *Z. anorg. allg. Ch.* 214, 196 (1933).
- [9] S. A. Shchukarev, E. Vol'f and M. P. Morozova, *J. Gen. Chem.* 24, 1925 (1954).*
- [10] F. Weibke and O. Kubaschewski, *Thermochemie der Legierungen*, Berlin (1943).
- [11] W. Bietz and N. Haase, *Z. allg. anorg. Ch.* 129, 141 (1923).
- [12] S. A. Shchukarev, G. Grossmann and M. P. Morozova, *J. Gen. Chem.* 25, 633 (1955).*
- [13] S. M. Ariia, M. P. Morozova, Huang Chi-t'ao and E. Vol'f, *J. Gen. Chem.* 27, 293 (1957).
- [14] S. A. Shchukarev, M. P. Morozova and Iu. P. Sapozhnikov, *J. Gen. Chem.* 26, 304 (1956).*

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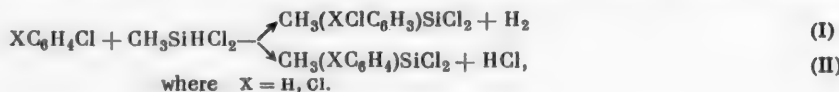
ON THE REACTIONS OF ALKYLDICHLOROSILANES WITH CHLORINATED HYDROCARBONS

S. N. Borisov, M. G. Voronkov and B. N. Dolgov

It is stated in the patent literature [1] that methyldichlorosilane reacts with chlorobenzene at 150-300° in the presence of 0.1-5 wt % of AlCl_3 or BCl_3 according to the scheme



At 450° the reaction between methyldichlorosilane and chlorobenzene does not require a catalyst [2]; however, the main reaction products are methylphenyldichlorosilane and methyltrichlorosilane. In the case of *p*-dichlorobenzene the isomeric methyl(chlorophenyl)dichlorosilanes are formed together with $\text{CH}_3(\text{C}_6\text{H}_4)\text{SiCl}_2$ and CH_3SiCl_3 . Evidently at high temperatures, in the absence of catalyst, reactions (I) and (II) occur concurrently,

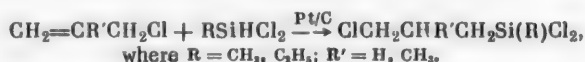


The formation of methyltrichlorosilane in these processes evidently arises as a result of the secondary reactions (III) and (IV).



At 525° in the presence of palladium the reaction of methyldichlorosilane with chloro- and trichlorobenzene [3] proceeds in the main according to scheme (II), giving $\text{CH}_3(\text{C}_6\text{H}_5)\text{SiCl}_2$ and $\text{CH}_3(\text{Cl}_2\text{C}_6\text{H}_3)\text{SiCl}_2$ respectively.

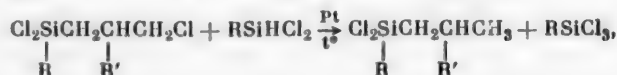
It was shown recently [4, 5] that on reaction of alkylchlorosilanes with alkyl and methallyl chlorides in the presence of 1% of platinum on charcoal at 160° the main effect is the addition



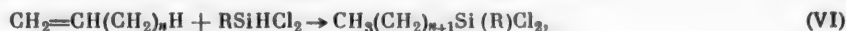
However, in addition to the γ -chloroalkylalkyldichlorosilanes, secondary products are also formed (alkyltrichlorosilanes and dialkyldichlorosilanes).

Under similar conditions the addition of alkylchlorosilanes to vinyl chloride [6] differs from their reaction with allyl chloride only in the direction of the addition (which in this case, in spite of Markovnikov's rule, leads to the formation of α -chloroethylalkyldichlorosilanes), not differing in principle in the nature of the secondary products. At the same time, according to Weinberg [7] the reaction of organodichlorosilanes ($\text{CH}_3\text{SiHCl}_2$, $\text{C}_6\text{H}_5\text{SiHCl}_2$, etc.) with excess vinyl chloride at 600° proceeds according to scheme (II) with the formation of compounds of the type $\text{R}(\text{CH}_2=\text{CH})\text{SiCl}_2$.

The supposition [4, 5] that the source of the by-products of the addition reaction between alkylchlorosilanes and allyl chloride is connected with secondary reactions of the type



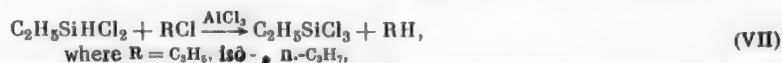
has not obtained experimental confirmation inasmuch as the reaction between γ -chloropropylethyldichlorosilane and ethyldichlorosilane did not lead, under addition-reaction conditions, to the formation of products in which hydrogen was exchanged for chlorine. Hence the formation of alkyltrichlorosilanes and dialkyldichlorosilanes in the reaction of RSiHCl_2 with halo-olefins is explained [5] by schemes (V) and (VI)



where $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n = 0 + 1$.

In view of the above considerations it was of definite interest to investigate the possibility of the reaction of scheme (V), which up to the present time has not been substantiated experimentally. With this objective we studied the reaction of ethyldichlorosilane with *n*-propyl, isopropyl and allyl chlorides.*

We have shown previously [8] that these chlorinated hydrocarbons in the presence of anhydrous aluminum chloride, even in the cold, readily undergo with triethylsilane an exothermic reaction of combined hydrogenation-halogenation; in this reaction the reaction rate and yield of triethylchlorosilane are determined mainly by the lability of the chlorine atom in the chlorinated hydrocarbon, in accordance with the series $\text{C}_3\text{H}_5\text{Cl} > \text{iso-C}_3\text{H}_7\text{Cl} > n\text{-C}_3\text{H}_7\text{Cl}$. In comparison with R_3SiH , the Si-H bond in RSiHCl_2 is less polarized ($\text{Si}^{\delta+}-\text{H}^{\delta-}$), which is reflected, for example, in its higher frequency in vibrational spectra and in its lower tendency towards heterolytic reactions.** The I-effect of the chlorine atoms decreases the hydride character of the hydrogen atom attached to silicon, deactivates the Si-H bond in RSiHCl_2 and, correspondingly, the exchange reaction between hydrogen and halogen. This is shown, in particular, by the fact that the reaction investigated by us

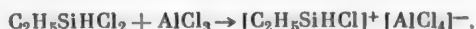


in the presence of 2-4 moles % of anhydrous aluminum chloride takes place extremely slowly at room temperature; it proceeds at a satisfactory rate only on heating the reaction mixture to 50-60°.***

From the data in the table it can be seen that in the case of isopropyl chloride in which the chlorine atom is more labile than in $n\text{-C}_3\text{H}_7\text{Cl}$, the conversion of ethyldichlorosilane to ethyltrichlorosilane is correspondingly higher. However, in the aliphatic series it is the reactivity of the Si-H bond that is the determining factor for reaction (VII) and not of the C-Cl bond. This is clearly indicated by the example of the reaction of ethyldichlorosilane with allyl chloride: as a result of the low activity of the Si-H bond in $\text{C}_2\text{H}_5\text{SiHCl}_2$ with respect to the hydrogen-chlorine exchange reaction, a secondary process predominates here - resin formation resulting from polymerization of the original allyl chloride and also of the propylene formed by the action of AlCl_3 , while only a third of the ethyldichlorosilane is converted to ethyltrichlorosilane.

It is important to note that in contrast to R_3SiH [8] the reaction of ethyldichlorosilane with RCl which takes place on addition of the chlorinated hydrocarbon to a mixture of ethyldichlorosilane and AlCl_3 does not occur with the reverse procedure - addition of $\text{C}_2\text{H}_5\text{SiHCl}_2$ to a mixture of RCl and AlCl_3 . The introduction of isopropyl chloride to a mixture of ethyldichlorosilane and aluminum chloride at room temperature does not give rise to any noticeable reaction; this begins only on heating the reaction mixture. At the same time, addition of $n\text{-C}_3\text{H}_7\text{Cl}$ to a mixture of $\text{C}_2\text{H}_5\text{SiHCl}_2$ and AlCl_3 , that has first been heated to boiling and then cooled to room temperature, gives rise to a slow exchange reaction.

Hence from an examination of the question of the scheme (VII) reaction mechanism it may be considered that a labile complex of ethyldichlorosilane and aluminum chloride is formed initially****



*It is known [4] that on addition of ethyldichlorosilane to allyl chloride the secondary products - RSiCl_3 and R_2SiCl_2 are formed in greatest quantity.

**This same fact results in a considerably higher reactivity of RSiHCl_2 and HSiCl_3 in comparison with R_3SiH in homolytic reactions of the S-H bonds. There are also other views on this question [9].

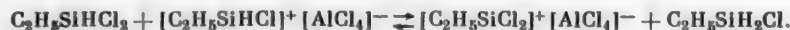
***In this connection it should be noted that although triethylsilane reduces *n*-butyltrichlorosilane in the presence of aluminum chloride, ethyldichlorosilane does not react under similar conditions [10].

****Investigation of the kinetics of disproportionation of the methylchlorosilanes in the presence of aluminum chloride has shown that in the reaction mixture the AlCl_3 occurs almost entirely in the form of complexes with the chlorosilanes [11].

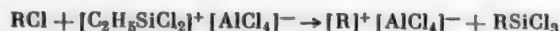
Reaction of Ethyldichlorosilane with Chlorinated Hydrocarbons
in the Presence of Aluminum Chloride

RCI	Molar ratio of C_2H_5- HCl_2 and RCI	Quantity of $AlCl_3$ (in moles % on $C_2H_5SiHCl_2$	Conversion of $C_2H_5SiHCl_2$ to $C_2H_5SiCl_3$ (in %)	Yield (in % calculated on the ethyl- dichlorosilane reacted)
C_3H_5Cl	1:1	4.0	32.5	73.8
iso- C_3H_7Cl	1:1.6	3.0	66.2	90.2
n- C_3H_7Cl	1:1	2.0	62.7	90.5

bringing about the conversion of ethyldichlorosilane to ethylchlorosilane



The halogenated hydrocarbons form more stable complexes with aluminum chloride [12, 13] that can favor the reaction



The $[R]^+ [AlCl_4]^-$ complex evidently cannot be reduced by ethyldichlorosilane in which the hydride character of the Si-H bond is weak. In ethylchlorosilane, however, the Si-H bond is evidently sufficiently active to reduce the complex.



The proposed reaction mechanism scheme explains satisfactorily the fact that there is no reaction on adding $RSiHCl_2$ to a mixture of alkyl chloride and aluminum chloride in which the latter occurs in the form of the comparatively stable complex $[R]^+ [AlCl_4]^-$.

EXPERIMENTAL

The ethyldichlorosilane was a product of b.p. 74.5-75.5°, prepared by fractionation of a technical mixture of ethylchlorosilanes through a glass column with a ceramic packing (efficiency, 40 theoretical plates). The organic halogenated derivatives were pure commercial preparations. The aluminum chloride was an anhydrous, purified material.

The experiments were carried out in an apparatus consisting of a three-necked flask fitted with a thermometer, dropping funnel and reflux condenser connected through a calcium chloride tube to a gasometer.

Reaction of Ethyldichlorosilane with Chlorinated Hydrocarbons

1. 15.7 g of iso- C_3H_7Cl was added over 20 minutes to a mixture of 25.8 g of ethyldichlorosilane and 0.53 g of $AlCl_3$. No reaction was observed at room temperature. Heating of the reaction mixture brought about a vigorous reaction accompanied by evolution of gas and exothermic heating of the mixture to 60°. On heating the mixture further a constant boiling point (91°) was rapidly established. On distilling the mixture 8.7 g of unreacted ethyldichlorosilane (33.7% of the original) and 19.5 g of ethyltrichlorosilane (90.2% calculated on the ethyldichlorosilane reacted) were obtained. The residue in the flask was a black, viscous resin. 2.1 liters of propane was collected during the course of the reaction.

2. A mixture of 19.5 g of ethyldichlorosilane and 0.6 g of $AlCl_3$ was heated to boiling and then cooled to room temperature. On addition of n-propyl chloride a slow reaction began, accompanied by evolution of gas. On heating the mixture to 60° the reaction proceeded vigorously. After 140 minutes of moderate heating the temperature of the reaction mixture reached 91° after which the reaction practically came to an end and further

addition of n-propyl chloride resulted only in lowering the boiling point of the mixture to 68.5°, and the evolution of gas practically ceased (2.6 liters of propane was collected). In all 18.6 g of n-propyl chloride was added, i.e., 150% of the necessary calculated quantity. On distillation of the reaction products 6.4 g of unreacted ethyldichlorosilane (37.3% of the original) and 14.0 g of ethyltrichlorosilane (90.5%) were obtained. The residue in the flask (1.5 g) was a black, viscous resin that solidified in the air.

3. After adding 19.4 g of ethyldichlorosilane, over a period of half an hour, to a boiling mixture of n-propyl chloride (23.5 g) and aluminum chloride (0.6 g) a constant boiling point of the mixture (49°) was established but no evolution of gas was observed. Further heating of the mixture for 1 hour brought about only resinification resulting evidently from secondary reactions of the alkyl halide with aluminum chloride. On distilling the reaction mixture the initial materials were obtained.

4. 15.3 g of allyl chloride was added over 90 minutes, with slight heating, to a mixture of 25.8 g of ethyldichlorosilane and 1.07 g of AlCl_3 , bringing about no noticeable reaction. The mixture was refluxed for a further 90 minutes and this led to a slow evolution of gas, rapid establishment of a constant boiling point (76°) and appreciable resinification of the mixture. On distilling the reaction products 2.25 g of unreacted allyl chloride, 17.4 g of unreacted ethyldichlorosilane (67.5% of the original) and 7.85 g of ethyltrichlorosilane (73.8% of the ethyldichlorosilane reacted) were obtained. The residue in the flask (7.4 g) was a viscous, black resin with an odor of naphtha (petroleum), becoming brittle in the air. The gas collected during the experiment, which amounted to 0.5 liter, was entirely absorbed by bromine (propylene).

The ethyltrichlorosilane obtained from the reactions between ethyldichlorosilane and chlorinated hydrocarbons had practically the same constants in all the experiments. After a second distillation it had the following constants.

B.p. 98.2°, n_D^{20} 1.4253, d_4^{20} 1.2393, M_R^D 33.76; calc. 33.78.

Found %: Cl 65.0, 65.2; Si 17.3. $\text{C}_2\text{H}_5\text{SiCl}_3$. Calculated %: Cl 65.05; Si 17.17.

SUMMARY

It is shown that in the presence of aluminum chloride ethyldichlorosilane takes part in a combined hydrogenation - halogenation reaction with chlorinated aliphatic hydrocarbons, reducing the latter to the corresponding hydrocarbons and being converted in the process to ethyltrichlorosilane.

LITERATURE CITED

- [1] U.S. Patent 2,499,561 (1950); Chem. Abs. 44, 5907 (1950); British Patent 669,219 (1952); Chem. Abs. 46, 7119 (1952).
- [2] British Patent 635,645 (1950); Chem. Abs. 44, 6882 (1950); U.S. Patent 2,511,820 (1950); Chem. Abs. 44, 8370 (1950); U.S. Patent 2,580,159 (1951); Chem. Abs. 46, 6670 (1952).
- [3] U.S. Patent 2,598,436 (1952); Chem. Abs. 47, 3875 (1953).
- [4] V. A. Ponomarenko, B. A. Sokolov, Kh. M. Minachev and A. D. Petrov, Proc. Acad. Sci. USSR 106, 76 (1956).
- [5] B. A. Sokolov, Dissertation, Moscow Chem.-Tech. Institute (1957).*
- [6] V. A. Ponomarenko, V. A. Sokolov and A. D. Petrov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 628 (1956).**
- [7] German Fed. Rep. Patent 936,445 (1955); Chem. Ref. J. 1957, 24,401; British Patent 752,700 (1956); Chem. Abs. 51, 7402 (1957); U.S. Patent 2,770,634 (1956); Chem. Abs. 51, 10560 (1957).
- [8] B. N. Dolgov, S. N. Borisov and M. G. Voronkov, J. Gen. Chem. 27, 716 (1957).**
- [9] M. I. Batuev, A. D. Petrov, V. A. Ponomarenko and A. D. Matveeva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1241 (1956).**
- [10] B. N. Dolgov, S. N. Borisov and M. G. Voronkov, J. Gen. Chem. 27, 2692 (1957).**

*In Russian.

**Original Russian pagination. See C.B. Translation.

- [11] P. D. Zemaný and F. P. Price, J. Am. Chem. Soc. 70, 4222 (1948).
- [12] N. N. Lebedev, Advances in Chemistry, 21, 1455 (1952).
- [13] U.S. Patent 2,676,933 (1954); Chem. Abs. 48, 9080 (1954).

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POLAROGRAPHY OF THE THERMAL DECOMPOSITION OF 2,2'-AZOBISISOBUTYRONITRILE IN VINYL BUTYL ETHER AND METHYL METHACRYLATE

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A number of works [1-7] are devoted to the decomposition of aliphatic azo compounds which are initiators of radical polymerization.

Most of the authors judged the rate of decomposition of the azo compounds investigated by the amount of nitrogen evolved. Bawn and Mellish [5] carried out the decomposition of the azo compound in a medium of brightly colored diphenyl- β -picrylhydrazyl free radicals which formed stable compounds with the radicals of the azo compound. The reaction was accompanied by a sharp change in the color of the solution. The cited authors checked the course of decomposition of the azo compound by a colorimetric method. Bevington, Bradbury and Burnett [7] used an isotopic indicator method for this purpose.

It was of interest also to use a polarographic method for study of the course of decomposition of azo compounds, 2,2'-azobisisobutyronitrile (ABN), in particular. Besides the direct determination of the decomposing azo compound at any stage of polymerization, we had in mind the possibility of simultaneously determining, firstly, nitriles [8] as deactivation products of azo-compound radicals, and secondly, the monomer in which the decomposition of the initiator takes place. Polarographic data thus obtained may also characterize the state of oxidation-reduction of the investigated medium during the polymerization process.

We carried out the decomposition of ABN in two media which sharply differed in their tendency toward polymer-chain formation. As a substance only slightly susceptible to radical polymerization with the initiator named, vinyl butyl ether was chosen; in contrast to this, as a substance which polymerizes intensely under similar conditions, methyl methacrylate was selected.

EXPERIMENTAL

The ABN used in the work was twice-recrystallized from purified methyl alcohol and had m.p. 101°; the methyl methacrylate was distilled beforehand, and the 100-101° fraction was used.

In the case of polymerization in solution 1 ml of a 0.5% solution of ABN in methyl methacrylate was mixed with an equal volume of a solvent consisting of a mixture of benzene and methyl alcohol (1:1) and placed in thin-walled, glass ampules. The sealed ampules were immersed in a water bath in which the temperature was automatically maintained at 60° with an accuracy of $\pm 0.1^\circ$. At half-hour intervals the ampules were taken out of the bath and crushed in a porcelain vessel containing a supporting electrolyte (2 ml of an aqueous solution of $(C_2H_5)_4NI + 2$ ml of ethyl alcohol). The solution obtained was poured into an electrolyzer and polarographed in order to determine its ABN content. After 100-fold dilution of this solution with supporting electrolyte, the methyl methacrylate content was determined polarographically.

In the case of mass polymerization a 0.1-0.5% solution of ABN in methyl methacrylate or vinyl butyl ether was poured into thin-walled glass ampules in amounts of about 1 g. The sealed ampules were kept at 60° in a water bath. After definite time intervals an ampule containing the solution being investigated was taken out of the water bath and put into a porcelain vessel containing 3 ml of ethyl alcohol. The ampule was crushed with a glass rod, and the contents of the vessel were thoroughly stirred. The alcoholic solution of ABN thus obtained was mixed with an equal volume of supporting electrolyte and put into the electrolyzer for polarographing.

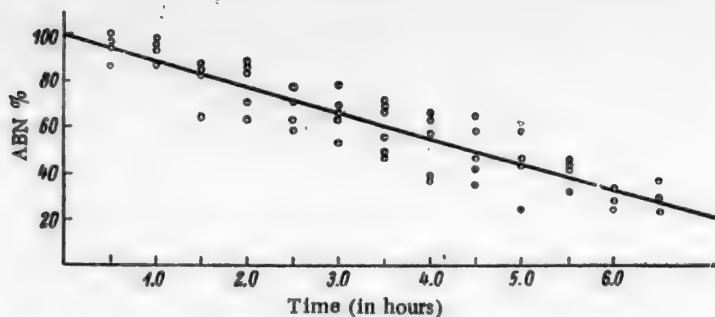


Fig. 1. Variation of quantities of 2,2'-azobisisobutyronitrile (ABN) in a solution of methyl methacrylate, benzene, and methyl alcohol (catalyst content 0.5% with respect to monomer).

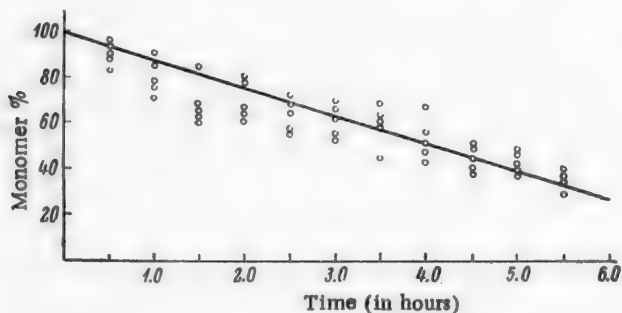


Fig. 2. Variation of quantities of methyl methacrylate on polymerization in a solution of benzene and methyl alcohol (catalyst content 0.5% with respect to monomer).

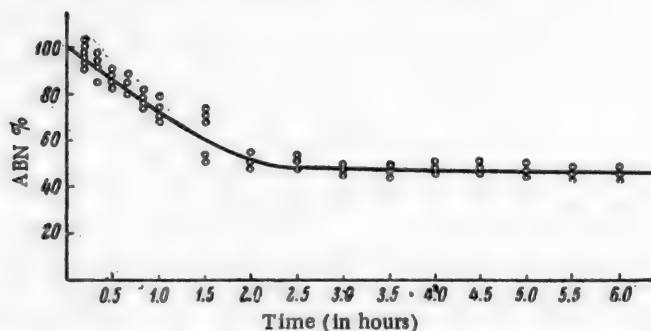


Fig. 3. Variation of quantities of 2,2'-azobisisobutyronitrile (ABN) en bloc with methyl methacrylate (catalyst content 0.5% with respect to monomer).

On polymerization of the methyl methacrylate under the conditions stated above, samples heated more than 2 hours had the form of a continuous, solidified, transparent mass. To extract ABN from solidified samples, the latter were pulverized in a special apparatus constructed by us for pulverizing polymer samples and, at the same time, extracting the unused initiator and monomer from them [9]. The alcoholic extract obtained was freed from fine particles of polymer, mixed with an equal volume of supporting electrolyte, and polarographed to determine ABN. To determine the amounts of methyl methacrylate not polymerized, we put 0.1-0.2 ml of the alcoholic extract into 5 ml of supporting electrolyte and again polarographed.

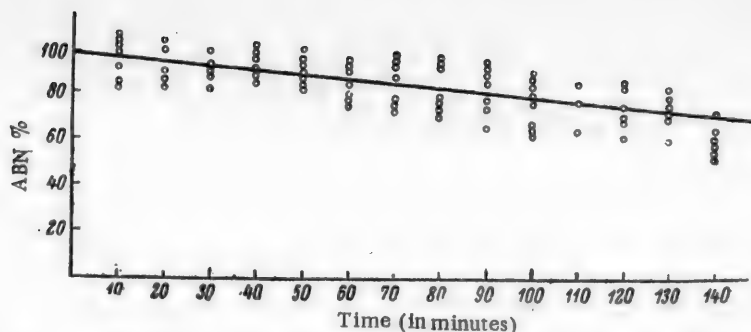


Fig. 4. Variation of quantities of 2,2'-azobisisobutyronitrile (ABN) en bloc with methyl methacrylate (catalyst content 0.1% with respect to monomer).

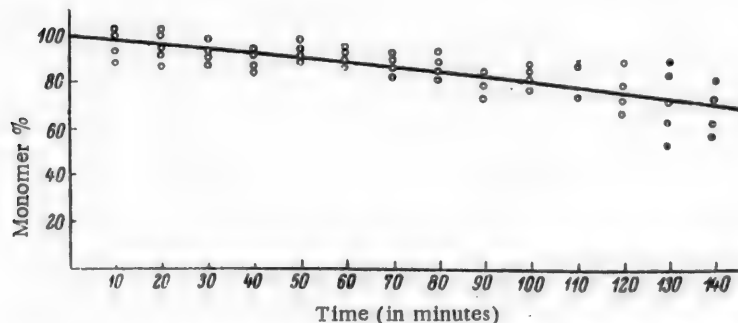


Fig. 5. Variation of quantities of methyl methacrylate on mass polymerization (catalyst content 0.1% with respect to monomer).

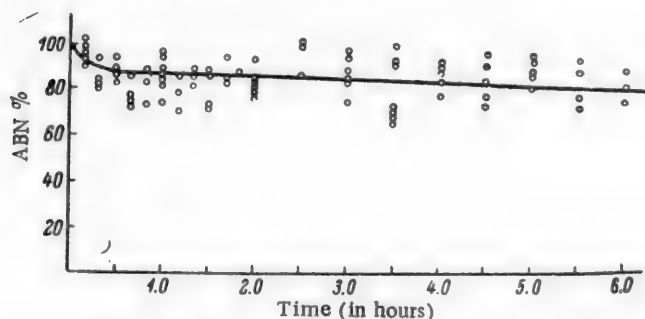


Fig. 6. Variation of quantities of 2,2'-azobisisobutyronitrile (ABN) en bloc with vinyl butyl ether (catalyst content 0.5% with respect to monomer).

The polarography was done by means of a Gor'kii M-7 polarograph with a mirror galvanometer, the current sensitivity of which was $I = 150 \text{ mm}/\mu\text{a}$. The measurements were made with a 1:10 shunt. The capillary was cylindrical and had a dropping period $t = 3 \text{ sec}$ and a drop weight $m = 0.34 \text{ mg}$; the capillary constant $m^2/s \cdot t^{1/2} = 1.83 \text{ mg}^2/s \cdot \text{second}^{-1/2}$ at 2.1 v. The height of rise of the mercury bulb provided for a possible decrease of tangential movements [10]. As supporting electrolytes, 50% aqueous-alcoholic solutions of $(\text{C}_2\text{H}_5)_4\text{NI}$ and LiCl were used.

On the basis of multiple measurements of the limiting diffusion currents due to reduction at the mercury drop of the ABN in initial samples and in samples corresponding to definite time intervals, the table and Figs. 1-6 were compiled. The change in the quantities of ABN during polymerization in vinyl butyl ether and methyl methacrylate, as well as the change in the amounts of monomer, may be estimated from these data.

Kinetics of Solution- and Mass Polymerization with 2,2'-Azobisisobutyronitrile as Catalyst (on the Basis of Polarographic Data)

Time from beginning of experiment (in hours)	Polymerization in methyl alcohol- benzene solution (1:1)		Mass polymerization		
	catalyst content with respect to methyl methacrylate (in %)				
	0.5		0.5		0.1
	decrease per 0.5 hour (in % of the initial quantity)				
	mono- mer	catalyst			monomer
0.5	6	6	12	8	6
1.0	8	7	16	5	5
1.5	5	6	12	5	6
2.0	5	5	—	4	5
2.5	7	5	10	—	—
3.0	5	5	0	—	—
3.5	6	5	0	—	—
4.0	6	5	0	—	—
4.5	7	6	0	—	—
5.0	5	5	0	—	—
5.5	5	5	0	—	—
6.0	7	5	0	—	—

DISCUSSION OF RESULTS

From consideration of the polarograms corresponding to the thermal decomposition of ABN and the subsequent consumption of the latter during polymerization in vinyl butyl ether it follows that in this case only reduction of ABN occurs. As we established earlier, the vinyl ether is not polarographed [11]. In the case of decomposition of ABN in methyl methacrylate two waves occur, of which the first corresponds to reduction of ABN and the second to reduction of methyl methacrylate.

From the obtained polarographic data on the change in the quantity of ABN when the content of the latter in the initial sample is 0.5%, it follows that the constant of thermal decomposition of ABN in a methyl methacrylate medium is $0.82 \cdot 10^{-4}$ (m/l) second⁻¹; in vinyl butyl ether it is $0.70 \cdot 10^{-4}$ (m/l) second⁻¹. Lewis and Matheson [1, 2], who determined the rate of decomposition of ABN in xylene at 80° by the quantity of nitrogen evolved, found a value for the constant of the same order, namely $1.53 \cdot 10^{-4}$ (m/l) second⁻¹.

As follows from the polarographic data obtained, the thermal decomposition of ABN is a first-order reaction. During the time interval under investigation (5-6 hours) the dependence of the methyl methacrylate content on time also is linear in character.

On solution polymerization (under the chosen experimental conditions) the change of viscosity with time is negligible, and the catalyst content, determined polarographically, changes uniformly in the course of the polymerization process during the entire period of time investigated. On mass polymerization the viscosity of the sample changes sharply in the course of time. For instance, in the case where the catalyst content is 0.5%, the sample hardens within 2.5 hours, and the change of catalyst content for each 0.5 hour, with respect to its initial value, during subsequent half-hour intervals is equal to zero.

On mass polymerization in vinyl butyl ether the ABN content becomes constant in the first 0.5 hour. On decomposition of the named initiator en bloc with methyl methacrylate, the ABN content becomes stable in 2.5 hours. When subsequent samples are polarographed, no change in ABN content is observed.

The rates of decrease of the quantity of ABN in methyl methacrylate, when the concentration of the former

is 0.1%, is considerably less than those for a concentration of 0.5%. It may be supposed that, in view of the lower rate of polymerization for an initiator concentration of 0.1%, which means also a lower rate of consumption of initiator radicals, the equilibrium of the reaction of thermal decomposition of ABN in this case is displaced to a lesser extent in the direction of radical formation.

SUMMARY

1. The possibility of using the polarographic method for the study of the course of the process of radical polymerization has been shown. The conditions for the polarographic determination of 2,2'-azobisisobutyronitrile on thermal decomposition of vinyl butyl ether and methyl methacrylate, as well as the simultaneous determination of methyl methacrylate, have been found.

2. The rate constant for the thermal decomposition of 2,2'-azobisisobutyronitrile in the named media has been determined by the polarographic method.

LITERATURE CITED

- [1] F. Lewis and M. Matheson, *J. Am. Chem. Soc.* **71**, 747 (1949).
- [2] F. Lewis and M. Matheson, et al, *J. Am. Chem. Soc.* **71**, 2610 (1949).
- [3] C. O. Overberger, M. T. O'Shaughnessy and Shalit, *J. Am. Chem. Soc.* **71**, 2661 (1949).
- [4] A. F. Bickel and W. A. Waters, *Rec. Trav. Chim.* **69**, 1490 (1950).
- [5] C. E. H. Bawn and S. F. Mellish, *Trans. Far. Soc.* **47**, 1216 (1951).
- [6] L. M. Arnett, *J. Am. Chem. Soc.* **74**, 2027 (1952).
- [7] J. C. Bevington, J. H. Bradbury and O. M. Burnett, *J. Polymer Sci.* **12**, 469 (1954).
- [8] M. I. Bobrova and A. N. Matveeva, *J. Gen. Chem.* **28**, 2929 (1958). *
- [9] M. I. Bobrova and A. N. Matveeva, *J. Gen. Chem.* **26**, 1857 (1956). *
- [10] T. A. Kriukova, *Ind. Lab.* **14**, 511 (1948).
- [11] M. I. Bobrova and A. N. Matveeva, *J. Gen. Chem.* **25**, 1741 (1955). *

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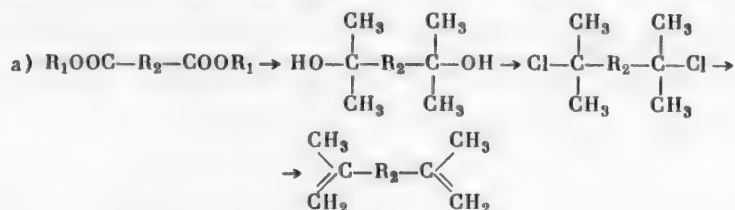
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PREPARATION OF CERTAIN COMPOUNDS WITH TWO ISOPROPENYL GROUPS

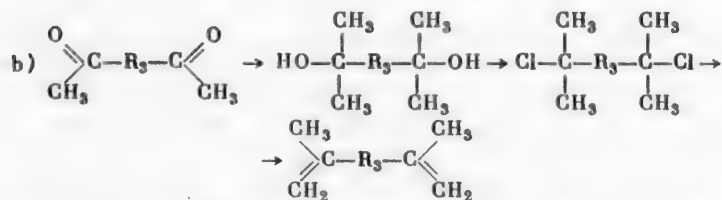
Iu. V. Mitin

Compounds containing two isopropenyl groups are of interest in connection with the development of a new method of polymer preparation [1]. However, there are practically no data in the literature, either on methods of synthesis or on the properties of these compounds. Only a method for the synthesis of p-diisopropenylbenzene is described [2], but this method is inconvenient for the preparation of appreciable quantities of product. Therefore a new, more efficient method of preparation of p-diisopropenylbenzene is proposed by us. As regards 4,4'-diisopropenylbiphenyl, 4,4'-diisopropenyldiphenylmethane, 4,4'-diisopropenyldiphenylethane, and 4,4'-diisopropenyldiphenyl ether, they are wholly unknown in the literature. True, 4,4'-diisopropenylbiphenyl is mentioned in the cited work [3], but apparently the authors were unable to obtain it in sufficiently pure form.

The over-all scheme of preparation of the final unsaturated compounds synthesized by us is as follows:



where $\text{R}_1 = \text{C}_6\text{H}_5$ or $n\text{-C}_3\text{H}_7$,



We rejected the direct dehydration of diols (by means of such catalysts as KHSO_4 , Al_2O_3 , etc.), which gives insignificant yields, and used a two-step method of preparation of unsaturated compounds through the corresponding dichlorides with subsequent splitting off of hydrogen chloride. Both steps — conversion to the chloride and splitting off of the hydrogen chloride — proceed with good yields (90-95%).

The synthesis according to scheme "a" was carried out in the case where the corresponding diketones were difficultly soluble or difficult to prepare. Such are p-diacetylbenzene and 4,4'-diacetylbiphenyl. Instead of diketones, therefore, it is more expedient to use the corresponding dicarboxylic acid esters, the solubility of which can be regulated by selecting the proper alkoxy groups. Carrying out the reaction of diacetyl derivatives or dicarboxylic acid esters with methylmagnesium bromide presents no difficulties; the diols are obtained in good

yield. Replacement of the hydroxyl group by a chlorine atom also proceeds smoothly. As a rule, the chlorides obtained are unstable compounds and readily split off hydrogen chloride even on standing.

The final products — diisopropenyl derivatives of benzene, biphenyl, diphenylmethane, etc.— are colorless, well-crystallized substances, stable on keeping for a short time.

On prolonged storage they may spontaneously polymerize to an insoluble, porous mass.

The structures, elementary analyses, and melting points of the substances obtained are given in the table.

The author thanks M. M. Koton, in whose laboratory the work was done, for valuable advice and interest in the work.

EXPERIMENTAL

1. Preparation of 1,4-diisopropenylbenzene (III). The starting material is diethyl terephthalate, which is much more soluble in ether and benzene than dimethyl terephthalate. To the Grignard reagent prepared from 20 g of magnesium and 95 g of methyl bromide was added dropwise a solution of 44.4 g of diethyl terephthalate in anhydrous benzene. After this the mixture was warmed for 1 hour in a water bath and then poured into a mixture of 400–500 g of ice and 200 g of ammonium chloride. The solvent was evaporated and the precipitated crystals were separated out, washed with water, dried, and recrystallized from benzene. Yield of pure 1,4-bis(α -hydroxyisopropyl)benzene (I), 24–25 g (66%).

Thirty g of substance (I) and 150 ml of benzene were put into a water-cooled Erlenmeyer flask and a current of dry hydrogen chloride passed into the mixture until the solid matter dissolved. The resulting solution of 1,4-bis(α -chloroisopropyl)benzene (II) was washed with water and 10% soda solution and dried with anhydrous calcium chloride. The solvent was distilled off in vacuo (without heating) or evaporated. The precipitated crystals were dissolved in petroleum ether. On cooling the solution to $(-30)^{\circ}$ – $(-40)^{\circ}$ fine crystals precipitated, which were immediately separated out, washed with a small amount of cooled petroleum ether, and dried in air. (However, recrystallization of the dichloride is not necessary for the next operation).

To prepare 1,4-diisopropenylbenzene the dichloride (II) was dissolved in 100 ml of pyridine and the solution boiled for 15 minutes. The mixture was poured into 0.5 l of cold water. The resulting precipitate was separated out and washed several times with water. The diisopropenylbenzene (III) formed was steam distilled and then recrystallized from alcohol, a small amount of activated charcoal being added. Yield of pure product, 18 g (75%, calculated on the basis of substance (I)).

2. Preparation of 4,4'-diisopropenylbiphenyl (VI). The starting material was propyl 4,4'-biphenyldicarboxylate (XV), m.p. 75° , prepared from 4,4'-biphenyldicarbonyl chloride and propyl alcohol. To prepare 4,4'-bis(α -hydroxyisopropyl)biphenyl (IV), 3.3 g of ester (XV), 1 g of magnesium, and 4 g of methyl bromide were used. The reaction was carried out similarly to the preparation of compound (I). The obtained (IV) was recrystallized from aqueous methyl alcohol. Yield, 18 g (65%).

4,4'-Bis(α -chloroisopropyl)biphenyl (V) was obtained in nearly quantitative yield by passing dry hydrogen chloride into a suspension of (IV) in benzene, recrystallized from hexane, and converted by heating with pyridine to 4,4'-diisopropenylbiphenyl (VI), which was crystallized from ethyl alcohol. Fine, shiny platelets, soluble in benzene, difficultly soluble in acetone and alcohols. Yield, 1 g (68%, calculated on the basis of substance (IV)).

3. Preparation of 4,4'-diisopropenyldiphenylmethane (IX). The starting material was 4,4'-diacetyldiphenylmethane (XVI), m.p. 92° (literature data: 93° [4]), 12.6 g of which was brought into reaction with the Grignard reagent prepared from 3 g of magnesium and 12 g of methyl bromide. 4,4'-Bis(α -hydroxyisopropyl)diphenylmethane (VII) was obtained in the form of a viscous liquid which split off water on distillation; therefore the product (VII) was converted without purification to 4,4'-bis(α -chloroisopropyl)diphenylmethane (VIII).

To split off hydrogen chloride, the obtained dichloride (VIII) was boiled with pyridine. The reaction product was recrystallized from ethyl alcohol, a little activated charcoal being added. Yield of substance (IX), 4.5 g (36%, calculated on the basis of substance (XVI)). Shiny leaflets, soluble in benzene and in carbon tetrachloride, difficultly soluble in alcohol.

4. Preparation of 4,4'-diisopropenyldiphenylethane (XII). The starting material was 4,4'-diacetyldiphenylethane (XVII), m.p. 167° (literature data: 168° [5]).

TABLE

Compound	Melting point	Calculated %			Found %		
		C	H	Cl	C	H	Cl
1,4-Bis(α -hydroxyisopropyl)benzene (I)	140° (1424)*	—	—	—	—	—	—
1,4-Bis(α -chloroisopropyl)benzene (II)*	68–69 Dec.	62.34	6.93	30.73	62.67	6.95	30.77
1,4-Diisopropenylbenzene (III)	64.5 (64)*	91.14	8.86	—	91.22	8.81	—
4,4'-Bis(α -hydroxyisopropyl)biphenyl (IV)*	161	80.00	8.15	—	80.04	8.38	—
4,4'-Bis(α -chloroisopropyl)biphenyl (V)*	114	70.35	6.51	23.13	70.48	6.66	23.00
4,4'-Diisopropenylbiphenyl (VI)	183	92.31	7.69	—	92.28	7.78	—
4,4'-Bis(α -hydroxyisopropyl)diphenylmethane VII*	Viscous liquid; splits off water on distillation						
4,4'-Bis(α -chloroisopropyl)diphenylmethane (VIII)*	Unstable liquid; readily splits off HCl						
4,4'-Diisopropenyl-diphenylmethane IX*	57	91.93	8.07	—	91.67	8.08	—
4,4'-Bis(α -hydroxyisopropyl)diphenyl-ethane (X)*	150	80.53	8.72	—	80.43	8.73	—
4,4'-Bis(α -chloroisopropyl)diphenyl-ethane (XI)*	119.5	71.64	7.16	21.19	71.21	7.70	21.24
4,4'-Diisopropenyl-ethane (XII)*	124.5	91.60	8.40	—	91.49	8.40	—
4,4'-Bis(α -hydroxyisopropyl)diphenyl ether (XIII)*	Viscous liquid; readily splits off water on distillation						
4,4'-Diisopropenyl-diphenyl ether (XIV)*	107.5	86.40	7.20	—	86.30	7.26	—

*Compounds marked with an asterisk were obtained for the first time.

** According to literature data [2].

4,4'-Bis(α -hydroxyisopropyl)diphenylethane (X) was prepared in the following manner: 14 g of diketone (XVII), 3 g of magnesium, 50 g of anhydrous benzene, and 25 ml of absolute ether were put into a round-bottom flask provided with stirrer, reflux condenser, and dropping funnel. A solution of 12 g of methyl bromide in 75 ml of absolute ether was added dropwise to the mixture. It was sometimes necessary, for activation, to add a few drops of methylmagnesium bromide solution. At the end of the reaction the mixture was heated for 1 hour more; it was then decomposed by a mixture of ice and ammonium chloride. The resulting substance (X) was recrystallized from benzene. Fine needles readily soluble in alcohols, difficultly soluble in benzene or ether. Yield, 10 g (64%).

4,4'-Bis(α -chloroisopropyl)diphenylethane (XI) was synthesized from 10 g of (X) by the method given above. It was recrystallized from hexane. Fine platelets, quite stable at room temperature. Readily soluble in almost all solvents. Yield, 9 g (82%).

4,4'-Diisopropenyldiphenylethane (XII) was prepared by heating dichloride (XI) with pyridine, as stated above. The product obtained was co-distilled with ethylene glycol and recrystallized from alcohol. Yield of pure product, 3.4 g (50%). Hydrocarbon (XII) is soluble in benzene and carbon tetrachloride, difficultly soluble in petroleum ether and acetone, and poorly soluble in alcohols.

5. Preparation of 4,4'-diisopropenyldiphenyl ether (XIV). The starting material was 4,4'-diacetyldiphenyl ether, m.p. 100° (literature data: 100-101° [6]), 62 g of which was brought into reaction with the Grignard reagent prepared from 12 g of magnesium and 50 g of methyl bromide. 4,4'-Bis(α -hydroxyisopropyl)diphenyl ether (XIII) was obtained in the form of a viscous liquid, which was placed in a distilling flask and heated at 100-140° (10 mm) until the evolution of water ceased. The residue was distilled in vacuo, and the 195-205° fraction (2 mm) was collected. The obtained substance (XIV) was recrystallized from alcohol. Shiny platelets, soluble in benzene and acetone, difficultly soluble in alcohol. Yield, 40 g (65%).

SUMMARY

1. A synthesis of 4,4'-diisopropenylbiphenyl, 4,4'-diisopropenyldiphenylmethane, 4,4'-diisopropenyldiphenylethane, and 4,4'-diisopropenyldiphenyl ether has been worked out.

2. The following compounds have been prepared and described for the first time: 1,4-bis(α -chloroisopropyl)benzene, 4,4'-bis(α -hydroxyisopropyl)biphenyl, 4,4'-bis(α -chloroisopropyl)biphenyl, 4,4'-bis(α -hydroxyisopropyl)diphenylmethane, 4,4'-bis(α -chloroisopropyl)diphenylmethane, 4,4'-diisopropenyldiphenylmethane, 4,4'-bis(α -hydroxyisopropyl)diphenylethane, 4,4'-bis(α -chloroisopropyl)diphenylethane, 4,4'-diisopropenyldiphenylethane, 4,4'-bis(α -hydroxyisopropyl)diphenyl ether, and 4,4'-diisopropenyldiphenyl ether.

3. The method of preparation of p-diisopropenylbenzene has been improved.

LITERATURE CITED

- [1] Iu. V. Mitin and N. A. Glukhov, Proc. Acad. Sci. USSR 15, 97 (1957). *
- [2] M. T. Bogert and C. P. Harris, J. Am. Chem. Soc. 41, 1676 (1919).
- [3] S. Patai and L. Rajbenbach, Bull. Research Council, Israel, 3, 46 (1953).
- [4] H. Duval, C. r. 146, 341 (1908).
- [5] R. C. Fuson and G. P. Speranza, J. Am. Chem. Soc. 74, 1621 (1952).
- [6] W. Dilthey, E. Bach, H. Grutering and E. Hausdorfer, J. pr. Ch. 117, 337 (1927).

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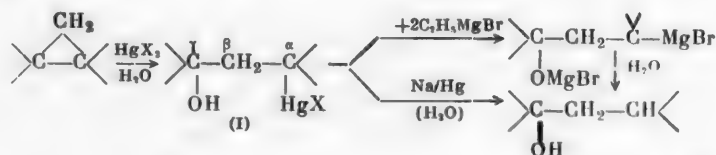
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INTERACTION OF CYCLOPROPANE HYDROCARBONS WITH MERCURIC SALTS

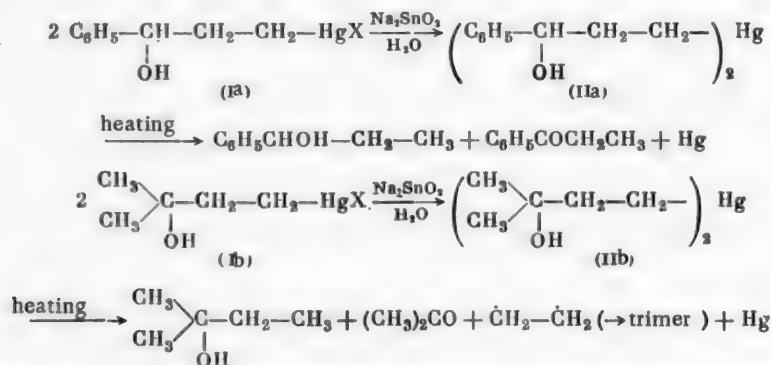
VIII. REACTION OF γ -MERCURATED ALCOHOLS WITH ZINC DUST

R. Ia. Levina and V. N. Kostin

In our earlier papers the reaction of alkyl- and arylcyclopropanes with mercury salts in aqueous solution [1-6], taking place with cleavage of the three-membered ring and leading to the formation of γ -mercurated alcohols (I), was described; the structure of the latter (and hence the position of ring cleavage) was established by their reduction (through replacement of the HgX group by hydrogen) and identification of the alcohols obtained thereby. The reduction of the γ -mercurated alcohols was carried out by treatment with sodium amalgam [1-4] or ethylmagnesium bromide [5, 6].

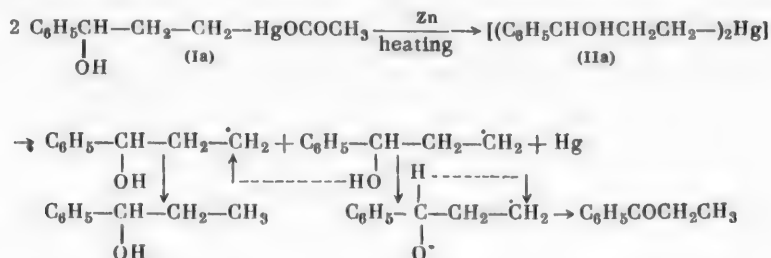


In order to avoid working with a large quantity of mercury (on reduction with sodium amalgam) or with diethylmercury (produced on reduction with ethylmagnesium bromide), we used another route for proof of the structure of γ -mercurated alcohols (Ia and Ib), which consisted in their symmetrization and the further decomposition of the resulting fully substituted organomercury compounds (IIa and IIb) containing alcohol groups in the γ -position relative to the mercury atom [7]. It was established that if the alcohol groups are secondary (IIa), thermal decomposition leads to the formation of an alcohol and a ketone, both having the carbon skeleton of the original fully substituted organomercury compound; if the alcohol groups in the γ -mercurated alcohol are tertiary (IIb), an alcohol with the same carbon skeleton is formed on thermal decomposition, while a ketone is also formed, owing to cleavage of the carbon-carbon bond; for instance:



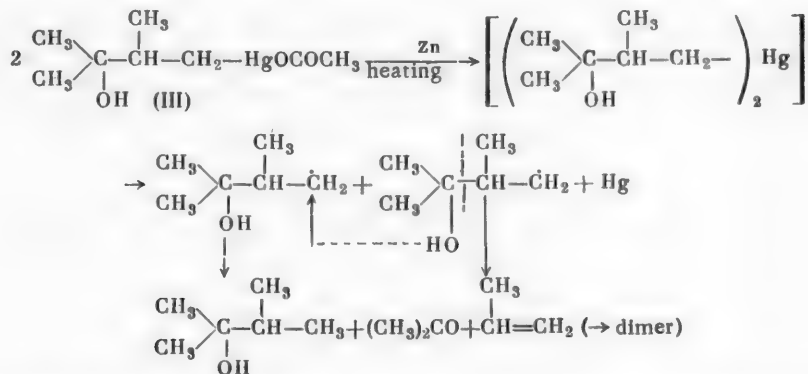
Since examples of symmetrization of organomercury salts by treatment with copper [8, 9] or zinc dust [9] are described in the literature, we attempted to symmetrize γ -mercurated alcohols (I) and to decompose thermally

the symmetrization products in one step by heating the γ -mercurated alcohols with zinc dust. Thus on determining the structure of γ -mercurated alcohols by the method of thermal decomposition it might be possible to dispense with the preliminary step of symmetrization. Actually it turned out that on heating 3-hydroxy-3-phenylpropylmercuric acetate (Ia), prepared from phenylcyclopropane [6], with zinc dust, there were formed ethylphenylcarbinol and ethyl phenyl ketone, i.e., the same reaction products whose formation we observed [7] in the thermal decomposition of di-(3-hydroxy-3-phenylpropyl)mercury (IIa).

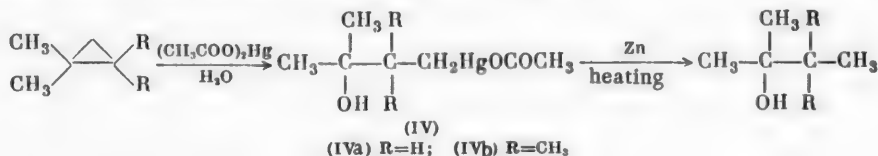


Confirmation of the given reaction mechanism (through the symmetrization step) was provided by the formation of ethylphenyl carbinol and ethyl phenyl ketone from the symmetrization product - di-(3-hydroxy-3-phenylpropyl)mercury (IIa) - on mild heating with zinc dust.

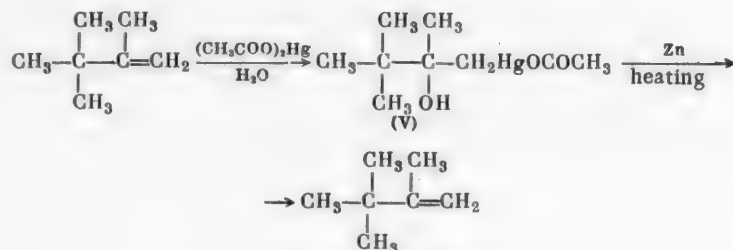
The reaction of thermal decomposition in the presence of zinc dust was studied further in the case of 3-hydroxy-2,3-dimethylbutylmercuric acetate (III), prepared from 1,1,2-trimethylcyclopropane. It was established that dimethylisopropylcarbinol (an alcohol having the carbon skeleton of the original organomercury compound), acetone, and propylene (and also a dimer of the latter) are formed from this γ -mercurated tertiary alcohol, i.e., that the decomposition is of the same type as that of the fully substituted organomercury compound (IIb) containing tertiary alcohol groups, investigated by us earlier [7]. Consequently the reaction proceeded according to the equation



As is evident from the above, the structure of γ -mercurated alcohols containing a tertiary alcohol group is most easily established, since the tertiary alcohol formed on reaction with zinc dust may be separated from the other decomposition products by distillation. This course - the separation of the tertiary alcohol from the products of reaction of γ -mercurated tertiary alcohols with zinc dust - was tested in the case of the 3-hydroxyalkylmercuric acetates prepared from 1,1-dimethylcyclopropane [5] and 1,1,2,2-tetramethylcyclopropane [1, 2]; in the first case, dimethylethylcarbinol was isolated; in the second, dimethyl-tert-butylcarbinol (triptanol).



Thus the thermal decomposition of γ -mercurated alcohols in the presence of zinc dust may serve as a simple (one step) and convenient method of determining their structure. A further attempt was made to apply the reaction with zinc dust to the β -mercurated alcohol (V) prepared by treating triptene, an olefin isomeric with tetramethylcyclopropane, with mercuric acetate. It was found that on distillation with zinc dust, β -mercurated alcohol (V) was converted to the original olefin; i.e., its behavior in this reaction was different from that of the isomeric γ -mercurated alcohol (IVb).



EXPERIMENTAL

Action of zinc dust on a γ -mercurated secondary alcohol on heating. Into a Wurtz flask with attached air condenser were put 39.5 g of 3-hydroxy-3-phenylpropylmercuric acetate (Ia) and 14 g of zinc dust. On mild heating there began a vigorous reaction in which the decomposition products were distilled off. After the distillation was completed, the distillate was separated from the small amount of mercury and redistilled. There was isolated a fraction with b.p. 212-220° (754 mm), n_D^{20} 1.5270, consisting of ethylphenylcarbinol (b.p. 210-212° at 758 mm, n_D^{20} 1.5257 [10]) and ethyl phenyl ketone (b.p. 215° at 750 mm, n_D^{20} 1.5270 [11]); yield 12 g (~90%). The presence of ethylphenylcarbinol and ethyl phenyl ketone in this fraction was ascertained by preparing the crystalline derivatives: α -phenylpropyl 3,5-dinitrobenzoate, m.p. 66-67° (from alcohol) and ethyl phenyl ketone 2,4-dinitrophenylhydrazone, m.p. 191-192° (from alcohol). According to literature data [7], these derivatives melt at 67 and 192°, respectively. A further product of symmetrization of 3-hydroxy-3-phenylpropylmercuric acetate - di-(3-hydroxy-3-phenylpropyl)mercury (IIa), 27 g [6] - was brought into reaction with zinc dust (8 g); on mild heating a vigorous reaction took place and decomposition products, (b.p. 214-221° at 754 mm, n_D^{20} 1.5260; yield 14 g, ~90%), whose composition included ethylphenylcarbinol (characterized by the 3,5-dinitrobenzoate, m.p. 66-67°) and ethyl phenyl ketone (characterized by the 2,4-dinitrophenylhydrazone, m.p. 191-192°), were distilled off.

Action of zinc dust on γ -mercurated tertiary alcohols on heating. 3-Hydroxy-2,3-dimethylbutylmercuric acetate (III). In a distilling apparatus, connected with a gas holder for the collection of evolved gas, were placed 118 g of 3-hydroxy-2,3-dimethylbutylmercuric acetate (prepared from 1,1,2-trimethylcyclopropane [3]) and 40 g of zinc dust. The mixture was cautiously heated until the reaction began, after which the heating was stopped; a violent reaction took place, in which gas was evolved and liquid decomposition products were distilled off. To complete the reaction, the reaction mixture was again heated; the collected distillate (23 g) was redistilled in the interval 50-120°. Repetition of the experiment with the same amounts of starting materials gave the same results. The evolved gas was passed into a vessel containing bromine; the dibromide obtained amounted to 8 g (12%); after the usual treatment and distillation it had the constants of 1,2-dibromopropane.

B.p. 140-141° (754 mm), n_D^{20} 1.5190. Literature data [12]; b.p. 139-140° (749 mm); n_D^{20} 1.5172.

On redistillation of the liquid distillate (46 g) three fractions were obtained: the first, b.p. 50-65°, 17 g; the second, b.p. 65-115°, 4 g; the third, b.p. 115-120°, 24 g. The acetone* contained in the first fraction was identified by preparing the 2,4-dinitrophenylhydrazone with m.p. 125-126°. The acetone was washed out of the first and second fractions by shaking with water; the separated hydrocarbon layer was washed with saturated potassium bisulfite solution, a solution of alkali, and water again and dried with calcium chloride. After distillation over sodium the isolated hydrocarbon - 6 g (44%) - had constants near those of 4-methylpentene-1 (one of the possible polymerization products of the split-off propylene).

* The appearance of acetone in the reaction product could be due not only to the decomposition of a γ -mercurated tertiary alcohol, but also to that of the zinc acetate formed.

B.p. 52-53° (740 mm), n_D^{20} 1.3838, d_4^{20} 0.6651. Dibromide: b.p. 86-89° (20 mm), n_D^{20} 1.4975, d_4^{20} 1.5680. Literature data for 4-methylpentene-1 [13]: b.p. 53.6-53.9°, n_D^{20} 1.3825, d_4^{20} 0.6646. Dibromide: b.p. 87° (21 mm), n_D^{20} 1.4980, d_4^{20} 1.5689.

The third fraction consisted of dimethylisopropylcarbinol (70% yield), b.p. 117-118° (745 mm); m.p. of the 3,5-dinitrobenzoate, 110-111° (a mixed sample with the 3,5-dinitrobenzoate of known dimethylisopropylcarbinol melted without depression).

Literature data [3]: b.p. 118-119° (760 mm); melting point of 3,5-dinitrobenzoate 110-111°.

3-Hydroxy-3-methylbutylmercuric acetate (IVa). On distillation of the product of the reaction between zinc dust and 3-hydroxy-3-methylbutylmercuric acetate (prepared from 1,1-dimethylcyclopropane [5]) there was isolated a fraction with b.p. 100-102°, which consisted of dimethylethylcarbinol; its 3,5-dinitrobenzoate melted at 117°.

Literature data [5]: b.p. 102-103° (756 mm); m.p. of dinitrobenzoate, 118°.

3-Hydroxy-2,2,3-trimethylbutylmercuric acetate (IVb). From the distillate obtained on heating this γ -mercurated alcohol (m.p. 69-70°; prepared from 1,1,2,2-tetramethylcyclopropane [1, 2]) with zinc dust, the crystal hydrate of dimethyl-tert-butylcarbinol (triptanol), m.p. 80° (after sublimation) was obtained on addition of water. Literature data: m.p. 81° [14].

Treatment of β -mercurated tertiary alcohol (V) with zinc dust. The reaction of 2-hydroxy-2,3,3-trimethylbutylmercuric acetate (7.5 g; prepared from triptene [2]) with zinc dust was carried out by the same method as for γ -mercurated alcohols. The reaction product was 2,3,3-trimethylbutene-1, (triptene), b.p. 77-78° at 750 mm, n_D^{20} 1.4015; yield 1.4 g (70%). Literature data [2]: b.p. 77.2-77.6° (748.5 mm), n_D^{15} 1.4030. The triptene obtained was characterized by the mercury derivative (obtained by treatment with mercuric acetate) with m.p. 101-102°.

SUMMARY

1. Treatment of γ -mercurated alcohols (3-hydroxyalkylmercuric acetates, prepared from cyclopropane hydrocarbons by reaction with mercuric acetate in aqueous solution) with zinc dust, with heating, may serve as a convenient method of determining their structure.

2. γ -Mercurated alcohols containing a secondary alcohol group give a secondary alcohol and a ketone, each having the carbon skeleton of the original organomercury compound.

3. γ -Mercurated alcohols containing a tertiary alcohol group form tertiary alcohols with the carbon skeleton of the original mercurated alcohol, while ketones are formed as a result of the cleavage of a carbon-carbon bond.

4. On heating a β -mercurated alcohol (prepared from triptene by treatment with mercuric acetate) with zinc dust the mercury salt is split off and the original olefin (triptene) is formed.

LITERATURE CITED

- [1] R. Ia. Levina and B. M. Gladshtein, Proc. Acad. Sci. USSR 71, 65 (1950).
- [2] R. Ia. Levina and V. N. Kostin, J. Gen. Chem. 23, 1054 (1953).*
- [3] R. Ia. Levina and V. N. Kostin, Proc. Acad. Sci. USSR 97, 1027 (1954).
- [4] R. Ia. Levina, V. N. Kostin and V. A. Tartakovskii, Moscow State Univ. Herald, Chem. No. 2, 77 (1956).
- [5] R. Ia. Levina, V. N. Kostin and V. A. Tartakovskii, J. Gen. Chem. 26, 2998 (1956).*
- [6] R. Ia. Levina, V. N. Kostin and V. A. Tartakovskii, J. Gen. Chem. 27, 881 (1957).*
- [7] R. Ia. Levina, V. N. Kostin and V. A. Tartakovskii, J. Gen. Chem. 27, 2049 (1957).*
- [8] Contardi and Clocca, Ann. ch. appl. 23, 362 (1933).
- [9] I. T. Eskin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 297, 302 (1942).

*Original Russian pagination. See C.B. Translation.

- [10] R. Vernimmen, *Bull. Soc. Chim. Belg.* 33, 98 (1924).
- [11] O. Wallach, *Lieb. Ann.* 332, 317 (1907).
- [12] Iu. K. Iur'ev, *J. Gen. Chem.* 9, 153 (1939).
- [13] C. G. Schmitt and C. E. Boord, *J. Am. Chem. Soc.* 54, 751 (1932).
- [14] A. E. Favorskii and E. Opel', *J. Russ. Chem. Soc.* 50, 67 (1918).

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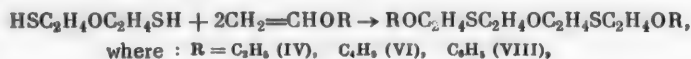
TABLE 1

Addition of Hydrogen Sulfide to Divinyl Ether in the Presence of 0.4 wt % of Azoisobutyronitrile (the Dinitrile of Azoisobutyric Acid) at 18-20°

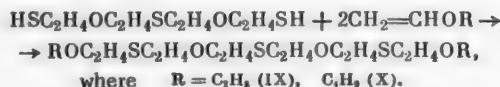
Ratio of divinyl ether and H ₂ S (in moles)	Reaction time (in days)	Yield of reaction products (in %)			
		I	II	III	total
1 : 4.2	29	31.4	27.6	22.5	81.5
1 : 8.5	14	47.4	26.7	16.6	90.6
1 : 5.1	42	41.0	26.1	18.5	85.6
1 : 4.3	20	33.5	28.9	28.4	90.8

Compounds (I-III), were obtained in the presence of a considerable excess of hydrogen sulfide; in this case the yields were directly proportional to the ratio of the starting materials, as follows from the data of Table 1.

Using an 8-fold excess of hydrogen sulfide, one can bring the yield of 2,2'-dimercaptodiethyl ether (I) up to 40-45%. Under the reaction conditions used by us, we did not observe the formation of cyclic or polymeric products: on varying the ratios of the starting materials, we were able to synthesize complex sulfide-dithiols (II, III) in considerable amounts. It is generally known [9] that such substances are by-products of the synthesis of dithiols by the reaction of dihalogen derivatives with hydrosulfides; however, the sulfide-thiols were not investigated by the cited authors. The dithiols synthesized by us were characterized in detail. In the case of the reaction of vinyl ethers with dithiols the latter displayed an even greater tendency toward similar addition to the double bond. In contrast to thiols, which in this reaction gave, depending on the experimental conditions, a mixture of anomalous and normal addition products [10], dithiols react strictly anomalously. In this reaction, which is exothermic, dithioethers are synthesized



and from sulfide-dithiol (II), correspondingly, trithioethers are formed



Complex compounds with mercuric chloride - crystalline substances - are obtained from di- and trithioethers. The degree of purity of the dithiol and sulfide-dithiols obtained was determined iodometrically by the usual method [11], slightly modified by us in that benzene was used as the solvent.

EXPERIMENTAL

The reaction between liquid hydrogen sulfide and divinyl ether was carried out in sealed ampules at 18-20° by a method described in detail earlier by us [1]. Divinyl ether: b.p. 28-28.5°, n_D^{20} 1.3982. As an example we shall describe Experiment 15. Fifteen g of the ether, 0.06 g of the dinitrile, and 64.5 g of liquid hydrogen sulfide were taken. The ampule was opened after 14 days. After removal of the excess hydrogen sulfide the increase in weight of the reaction mass amounted to 12 g. On fractional distillation the following fractions were obtained: the first, 64-65° (2 mm), 14.6 g; the second, 168-170° (2.5 mm), 7.2 g. The residue - a colorless, viscous fraction - amounted to 4.3 g. The first fraction was completely redistilled at 64-65° (2 mm) and consisted of 2,2'-dimercaptodiethyl ether (I).

B.p. 64-65° (2 mm), 71-72° (4 mm), n_D^{20} 1.5214, d_4^{20} 1.1138, M_{rD} 37.82; calculated 37.69. Literature data: b.p. 103-104° at 18 mm, n_D^{20} 1.5339, d_4^{20} 1.1854, d_4^{25} 1.1648 [9]; b.p. 217° [12], b.p. 53-54° (0.05 mm), d_4^{20} 1.127 [11]; b.p. 95-95.3° (12.7 mm) [13].

Found % C 34.80, 34.76; H 7.26, 7.28; S 45.95, 46.17. C₄H₁₀OS₂. Calculated % C 34.75; H 7.29; S 46.39.

TABLE 2

No. of experiment	Starting materials (in g)		Azoisobutyronitrile dinitrile of azoisobutyric acid (in g)	Temperature rise to	Duration of experiment (in days)	Yield of dithioether (IV) (in %)
	dithiol (I)	vinyl ethyl ether				
1a	5.6	16	0.025	—	27	87.3
2	4	12.6	0.01	25°	3	90.6
3	2.5	3	—	40	3	88.6

(I) reacted with an alcoholic solution of mercuric chloride with splitting-off of HCl. However, the reaction was not quantitative, and the corresponding dimercurichloride was not isolated. The 2,2'-dimercaptodiethyl ether (I) was 100% pure (according to iodometric titration).

The second fraction distilled at 165-167° (2 mm) and consisted of the corresponding sulfide-dithiol (II):

B.p. 165-167° (2.5 mm), 170-174° (3-3.5 mm), 164-166° (2 mm), n_D^{20} 1.5380, d_4^{20} 1.1574, MR_D 65.51; 65.78. Literature data: b.p. 182-185° (8 mm) [9].

Found %: C 39.53, 39.40; H 7.47, 7.35; S 39.38, 39.43. $C_8H_{12}O_2S_3$. Calculated %: C 39.62; H 7.49; S 39.68.

Sulfide-dithiol (II), a clear, colorless liquid, soluble in all organic solvents, had a less sharp odor and gave instantaneously a qualitative reaction with mercuric chloride in the presence of methyl orange. The sulfide-dithiol (II) was 99.5-99.8% pure (by iodometric titration).

The third fraction, a colorless, oily, rather viscous liquid, did not distill; it was practically insoluble in alcohol, ether, and acetone and readily soluble in benzene. It gave an acid reaction in the presence of methyl orange on addition of an alcoholic solution of mercuric chloride, which indicated that a molecule of this substance contains free thiol groups. The fraction was analyzed without additional purification and apparently consisted of somewhat impure sulfide-dithiol (III). Actually, iodometric determination of this preparation gave 94-95% purity.

Found %: C 42.60, 42.73; H 7.54, 7.53; S 36.15, 35.92. $C_{12}H_{26}O_3S_4$. Calculated %: C 41.59; H 7.56; S 37.01.

Reaction of dithiol (I) with vinyl ethers. The reaction between vinyl alkyl ethers and dithiol (I) took place even without catalyst when the initial reagents were mixed, but it proceeded with exceptional vigor in the presence of the catalyst (dinitrile).

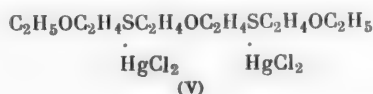
a) (I) + vinyl ethyl ether → (IV). The conditions and results of certain experiments are given in Table 2.

After the excess vinyl ethyl ether was driven off, the reaction product consisted of a single substance — bis-[2-(ethoxyethyl)-(2-thioethyl)] ether (IV).*

B.p. 176-177° (3 mm), 171-173° (2-2.3 mm), 164° (1.5 mm), n_D^{20} 1.4899, d_4^{20} 1.0399, MR_D 78.52; 78.48.

Found %: C 50.99, 51.27; H 9.27, 9.25; S 22.48, 22.35. $C_{12}H_{26}O_3S_2$. Calculated %: C 51.02; H 9.28; S 22.7.

Dithioether (IV) is a colorless, oily liquid without any sharp odor, soluble in all organic solvents. (IV) reacted vigorously with an alcoholic solution of $HgCl_2$, giving a neutral reaction in the filtrate in the presence of methyl orange and a quantitative yield of complex compound (V) in the precipitate.



*A. E. Kretov [14] isolated a fraction with b.p. 200-220°, corresponding to the composition of the dithioether, from the by-products.

It crystallized from a concentrated solution in hot alcohol in the form of acicular crystals with m.p. 80.5-80.7°.

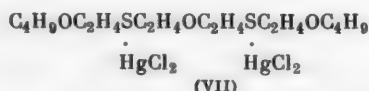
Found % C 17.10, 17.17; H 3.09, 3.06; Cl 17.39, 17.14. $C_{12}H_{23}O_2S_2Hg_2Cl_4$. Calculated % C 17.46; H 3.18; Cl 17.18.

b) (I) + vinyl butyl ether \rightarrow (VI). When 6 g of dithiol (I), 0.03 g of the dinitrile, and 20 g of vinyl butyl ether were mixed, the temperature rose to 65°. From the reaction product, 12.5 g (85%) of bis-[2-(butoxyethyl)-(2-thioethyl)] ether (VI) was isolated at 207-208° (3 mm).

B.p. 207-208° (3 mm), 186-188° (1.3-1.5 mm), n_D^{20} 1.4820, d_4^{20} 0.9714, MR_D 97.0; calc. 96.9.

Found % C 56.56, 56.53; H 10.04, 10.00; S 19.13, 18.90. $C_{16}H_{34}O_3S_2$. Calculated % C 56.76; H 10.12; S 18.94.

In the reaction with $HgCl_2$, (VI) behaved like (IV). Complex compound (VII), m.p. 71°, was isolated.



Found % C 22.05, 22.08; H 3.78, 3.71; Cl 16.28, 15.92. $C_{16}H_{34}O_3S_2Hg_2Cl_4$. Calculated % C 21.80; H 3.89; Cl 16.09.

c) (I) + vinyl phenyl ether \rightarrow (VIII). On mixing 4.5 g of (I) with 8 g of vinyl phenyl ether in the presence of 0.01 g of the dinitrile, the temperature of the reaction mass rose to 43°. The product remained clear and viscous for a long time and then crystallized. After several washings with alcohol the product was isolated quantitatively: m.p. 61.5° after crystallization from boiling ethanol.

Found % C 63.59, 63.60; H 6.83, 6.89; S 16.90, 16.93. $C_{20}H_{26}O_3S_2$. Calculated % C 63.46; H 6.92; S 16.94.

d) (I) + divinyl ether. The behavior of divinyl ether proved to be peculiar. At room temperature it was impossible to obtain an individual addition product as in the case of other vinyl ethers. A viscous product of polymeric character was obtained, which dissolved readily in benzene and was precipitated by ether, m.p. 46°; on analysis it was found to contain 36% sulfur, but it was not investigated in detail.

Reaction of sulfide-dithiol (II) with vinyl ethers. On mixing the initial reagents the temperature rose to 40° within 25-35 minutes.

a) (II) + vinyl ethyl ether \rightarrow (IX). From 3.6 g of (II) and 3 g of vinyl ethyl ether in the presence of 0.01 g of the dinitrile there was isolated the fraction: 215-230° (2-2.5 mm), n_D^{20} 1.5056 in the amount of 5 g, or 87.7% of the desired trithioether (IX). After repeated fractional distillation it had the following constants:

B.p. 231-234° (2 mm), n_D^{20} 1.5060, d_4^{20} 1.0781, MR_D 106.5; calc. 106.5.

Found % C 49.88, 49.77; H 8.82, 8.94; S 25.10, 24.96. $C_{16}H_{34}O_4S_3$. Calculated % C 49.70; H 8.86; S 24.88.

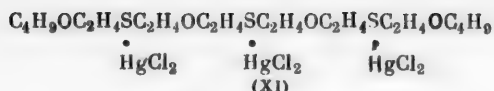
On interaction with mercuric chloride in the presence of methyl orange, (IX) gave a neutral reaction; however, the precipitated complex compound could not be obtained in pure form.

b) (II) + vinyl butyl ether \rightarrow (X). From 2.5 g of (II) and 3 g of vinyl butyl ether in the presence of 0.01 g of the dinitrile, 4.1 g (89.9%) of the desired trithioether (X) was obtained.

B.p. 245-250° (2-2.5 mm), n_D^{20} 1.4987, d_4^{20} 1.0372, MR_D 125.25; calc. 125.04.

Found % C 54.35, 54.24; H 9.58, 9.58; S 22.00, 21.94. $C_{20}H_{42}O_4S_3$. Calculated % C 54.26; H 9.56; S 21.73.

On interaction of trithioether (X) with $HgCl_2$ the filtrate gave a neutral reaction in the presence of methyl orange. Complex compound (XI), m.p. 75°, was obtained in quantitative yield.



Found %: C 19.07, 19.27; H 3.29, 3.21; Cl 16.89, 16.68. $\text{C}_{20}\text{H}_{42}\text{O}_4\text{S}_3\text{Hg}_3\text{Cl}_6$. Calculated %: C 19.10; H 3.37; Cl 16.92.

SUMMARY

1. The reaction between divinyl ether and a considerable excess of liquid hydrogen sulfide has been studied; substances having a linear structure — a dithiol and sulfide-dithiols — have been synthesized.
2. Certain transformations of the dithiol and a sulfide-dithiol have been investigated; in the case of the reaction with vinyl ethers it has been shown that they have an even greater tendency toward anomalous addition to the double bond than thiols.
3. Certain dithioethers and trithioethers have been synthesized; complex compounds of these with mercuric chloride have been obtained.

LITERATURE CITED

- [1] M. F. Shostakovskii, E. N. Prilezhaeva and E. S. Shapiro, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 292, 303 (1954).*
- [2] M. F. Shostakovskii, E. N. Prilezhaeva and E. S. Shapiro, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 734, (1955).*
- [3] M. F. Shostakovskii, E. S. Shapiro and F. P. Sidel'kovskaia, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 68 (1958).*
- [4] M. F. Shostakovskii and E. V. Dubrova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 339 (1958).*
- [5] M. F. Shostakovskii, A. V. Bogdanova, G. I. Plotnikova and E. V. Dubrova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 756, (1958).*
- [6] D. Harman and W. E. Vaughan, *J. Am. Chem. Soc.* 72, 631 (1950).
- [7] U.S. Patent No. 2514661 (1950).
- [8] U.S. Patent No. 2522590 (1950).
- [9] N. B. Tucker and E. E. Reid, *J. Am. Chem. Soc.* 55, 775 (1933); J. R. Meadow and E. E. Reid, *l. c.* 56, 2177 (1934); W. Hall and E. E. Reid, *l. c.* 65, 1466 (1943).
- [10] M. F. Shostakovskii, E. N. Prilezhaeva and E. S. Shapiro, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 357 (1953).*
- [11] J. W. Kimball, R. L. Kramer and E. E. Reid, *J. Am. Chem. Soc.* 43, 1199 (1921); S. D. Simpson, *Can. J. Research*, 25 B, 20 (1947).
- [12] H. J. Backer and F. Stienstra, *Rec. trav. chim.* 52, 1033 (1933).
- [13] C. M. Hall, L. Weinland, S. R. Olsen and W. G. Frame, *Ind. Eng. Ch.* 40, 513 (1948).
- [14] A. E. Kretov, *J. Russ. Chem. Soc.* 61, 2369 (1929).

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FROM THE FIELD OF ORGANIC INSECTOFUNGICIDES

XXXVI. ON THE REACTION OF TETRACHLORO- AND PENTACHLOROCYCLOPENTADIENES WITH CERTAIN UNSATURATED COMPOUNDS*

N. N. Mel'nikov and S. D. Volodkovich

In connection with the discovery of the insecticidal properties of polychloro-derivatives of polycyclic hydrocarbons in recent years, the condensation of hexachlorocyclopentadiene with various unsaturated hydrocarbons has been studied in a great number of cases, and certain compounds of this type have found wide application in agriculture, for vegetable-pest control [1-3]. The condensation of 2,3,4,5-tetrachlorocyclopentadiene and 1,2,3,4,5-pentachlorocyclopentadiene with unsaturated compounds was studied only in the cases of cyclopentadiene, maleic anhydride, benzoquinone, and acrylonitrile [4-6].

The synthesis of the adducts of 2,3,4,5-tetrachlorocyclopentadiene and 1,2,3,4,5-pentachlorocyclopentadiene with various unsaturated compounds and the study of their insecticidal properties is of great interest both for the purpose of obtaining data concerning the dependence of insecticidal activity on structure and for that of collecting material for elucidation of the mechanism of the action of the given group of compounds on insects. It was especially interesting to compare the insecticidal activity of the fluorine-containing analogs of 'aldrin,' recently described by us, with that of compounds containing hydrogen and one halogen atom in the endomethylene bridge.

In connection with the above a special investigation of the synthesis and study of the products of condensation of 2,3,4,5-tetrachlorocyclopentadiene and 1,2,3,4,5-pentachlorocyclopentadiene with unsaturated compounds, primarily bicyclo-[2,2,1]-heptene, bicyclo-[2,2,1]-heptadiene-2,5, maleic acid esters, and certain other substances. The compounds prepared by us and their properties are given in the table.

The condensation of 1,2,3,4,5-pentachlorocyclopentadiene and 2,3,4,5-tetrachlorocyclopentadiene with unsaturated hydrocarbons and esters of unsaturated acids takes place, almost the same as in the case of hexachlorocyclopentadiene, on heating a mixture of the reacting substances to 110-130° for several hours.

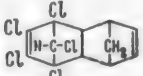
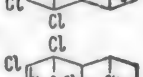
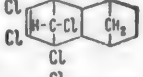
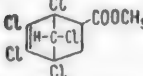
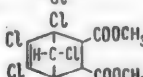
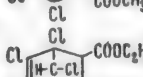
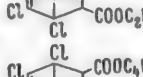
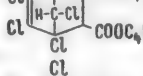
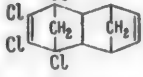
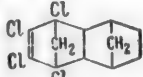
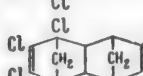
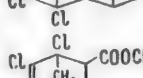
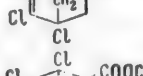
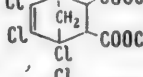
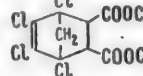
The study of the insecticidal effects of various substances on house flies, carried out by E. F. Granin under the direction of K. A. Gar, showed that the most active insecticide is 1,2,3,4,10-pentachloro-1,4,5,8-diendomethylenhexahydronaphthalene [1], which has nearly twice the insecticidal activity of chloroindane, but is inferior to 'aldrin.' 1,2,3,4-Tetrachloro-1,4,5,8-diendomethylenhexahydronaphthalene is practically inactive. These observations give a direct indication of the great effect on the toxicity of 'aldrin'-type compounds of substituents in the endomethylene bridge, which was noted by us also in the study of the corresponding fluoro-derivatives [7].

EXPERIMENTAL

Preparation of starting materials. 2,3,4,5-Tetrachlorocyclopentadiene was prepared by us by reduction of hexachlorocyclopentadiene with zinc dust in acetic acid [4, 8]. After recrystallization from methyl alcohol the 2,3,4,5-tetrachlorocyclopentadiene had m.p. 61-62°.

1,2,3,4,5-Pentachlorocyclopentadiene was obtained by the fractionation of technical hexachlorocyclopentadiene prepared by the chlorination of cyclopentadiene with sodium hypochlorite, and also by the reduction of C_6Cl_8 with $SnCl_2$ in acetone. 1,2,3,4,5-Pentachlorocyclopentadiene had the following constants.

*From the master's thesis of S. D. Volodkovich.

No. of compound	Formula	Boiling point (pressure in mm)	Melting point	n_D^{20}	d_4^{20}	MR		Yield (in %)	Chlorine content (in %)	
						found	calculated		found	calculated
1	 a)	172—173° (10)	—	1.5752	1.4970	72.85	72.21	70	53.47	53.70
	 b)	—	82—83	—	—	—	—	15	63.51	—
2		—	93—94	—	—	—	—	60	53.84 54.22	53.38
3		135—136 (4)	—	1.5375	1.5912	63.87	64.76	70	54.92 54.22	54.69
4		184—185 (4)	88—89	—	—	—	—	39	46.03 45.65	46.40
5		168—169 (4)	—	1.5410	1.5292	84.23	84.77	34	43.81 43.45	43.11
6		175—176 (4)	122—123	—	—	—	—	34	37.38 36.88	37.94
7		142—143 (4)	—	1.5620	1.4278	67.68	67.35	43	48.44 48.58	47.97
8		140—141 (4)	—	1.5630	1.4170	68.35	67.81	47	47.37 47.63	47.65
9		208—210 (24)	—	1.5442	1.4180	79.25	78.73	54	39.87 40.48	39.88
10		146—147 (20)	—	1.5300	1.4947	59.82	59.90	50	49.43 49.25	48.96
11		—	105—106	—	—	—	—	43	40.91 41.29	40.80
12		163—194	—	1.5349	1.4534	80.45	79.90	37	37.05 36.50	37.76
13		174—176	—	1.5210	1.3644	89.85	89.13	31	35.00 34.31	35.15
14		188—190	—	1.5060	1.3141	97.67	98.36	32	32.29 33.00	32.87

B.p. 104-106° (23 mm), d_4^{20} 1.6642, n_D^{20} 1.5615, M_R 46.62; calc. 46. 48.

Condensation of polyhalocyclopentadienes with unsaturated compounds. The condensation of 1,2,3,4,5-pentachlorocyclopentadiene and 2,3,4,5-tetrachlorocyclopentadiene with unsaturated compounds was carried out by heating equimolar quantities of the reagents in a flask provided with a reflux condenser and a mechanical stirrer. Reaction temperature, 120-130°. Duration, 3-4 hours.

In the condensation of polychlorocyclopentadienes with bicyclo-[2,2,1]-heptadiene-2,5, a 2.5-fold excess of the latter was used.

The condensation of 2,3,4,5-tetrachlorocyclopentadiene with esters of maleic acid was carried out in toluene by boiling the solution for 6-8 hours.

The compounds prepared by us and their properties are given in the table.

SUMMARY

1. The reactions of 2,3,4,5-tetrachloro- and 1,2,3,4,5-pentachlorocyclopentadienes with certain unsaturated compounds have been studied. It has been shown that these reactions go smoothly under the same conditions as the reactions of unsaturated compounds with hexachlorocyclopentadiene. A number of tetra- and pentachloro-derivatives of polycyclic compounds, not described in the literature, have been synthesized.

2. The study of the insecticidal activity of the synthesized compounds showed that the toxicity of 'aldrin'-type compounds is greatly affected by substituents in the endomethylene bridge. The insecticidal activity decreases in the order: dichloro-, monochloro-, difluoro-derivatives.

Of the synthesized compounds not described in the literature, 1,2,3,4,10-pentachloro-1,4,5,8-diendomethylenehexahydronaphthalene has the highest insecticidal activity, being nearly twice as active as chloroindane, but inferior to 'aldrin.'

LITERATURE CITED

- [1] N. N. Mel'nikov and L. G. Vol'fon, *Chem. Ind.* 10, 45 (1953).
- [2] L. G. Vol'fon, *Chem. Means Prot. Veg.* 2, 23 (1957).
- [3] L. G. Vol'fon, N. N. Mel'nikov, A. F. Plate, Iu. N. Sapozhkov and G. S. Taits, *Proc. Acad. Sci. USSR* 105, 1252 (1955).
- [4] E. McBee, R. Meyers and C. Baranauskas, *J. Am. Chem. Soc.* 77, 86 (1955).
- [5] A. Roedig and L. Hornig, *Ber.* 88, 2003 (1955).
- [6] E. McBee and D. Smith, *J. Am. Chem. Soc.* 77, 389 (1955).
- [7] S. D. Volodkovich, N. N. Mel'nikov, A. F. Plate and M. A. Prishnikova, *J. Gen. Chem.* 28, 3123 (1958).
- [8] A. A. Danish, M. Silverman and Y. Tayima, *J. Am. Chem. Soc.* 76, 6144 (1954).

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Insectofungicides

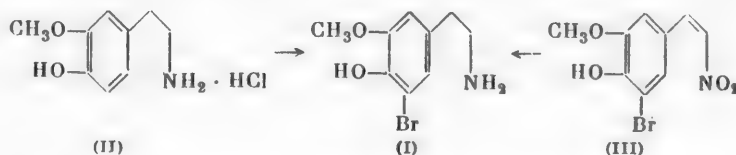
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SYNTHESIS OF BROMO-SUBSTITUTED β -PHENYLETHYLAMINES

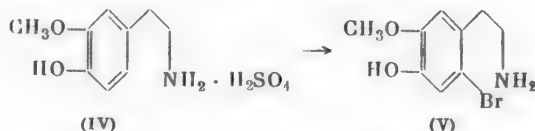
O. N. Tolkachev, V. G. Voronin and N. A. Preobrazhenskii

β -(3-Methoxy-4-hydroxy-5-bromophenyl)ethylamine (I) is an important intermediate in the synthesis of the dimethyl ether of the racemic alkaloid, tubocurarine iodide [1]. The preparation of substances of analogous structure is a laborious, multistage process resulting in low yield [2-4]. Although the direct halogenation of compounds containing a vanillyl radical is described in the literature, the question of orientation on bromination in such molecules remains insufficiently clear. In connection with this it is definitely of interest to work out the conditions of bromination of substituted β -phenylethylamines in order to prepare the required bromo-derivatives.

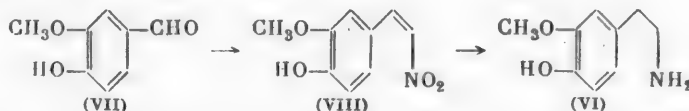
A number of authors have shown that eugenol [5], isoeugenol [6-7], and olivil [8] give 5-bromo derivatives while creosol [9, 10] and homovanillic acid [11], as well as the corresponding dimethoxy, dibenzyloxy, and other derivatives, give 6-bromo isomers [12-18]. Thus the most probable position on bromination is C₅ or C₆. Actually, when the reaction is carried out without solvent, a mixture of these isomers and an insignificant amount of the dibromo derivative are formed. Practically pure β -(3-methoxy-4-hydroxy-5-bromophenyl)ethylamine (I) is obtained by the bromination of β -(3-methoxy-4-hydroxyphenyl)ethylamine hydrochloride (II) in acetic acid solution. An identical substance (according to melting point and ultraviolet spectrum) was obtained also by the reduction of 3-methoxy-4-hydroxy-5-bromo- ω -nitrostyrene (III) with lithium aluminum hydride.



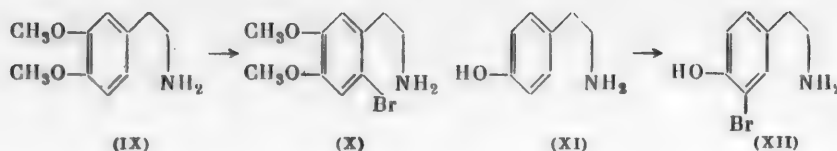
We found also that the bromination of β -(3-methoxy-4-hydroxyphenyl)ethylamine acid sulfate (IV) under similar conditions leads to the 6-bromo isomer (V).



The required β -(3-methoxy-4-hydroxyphenyl)ethylamine (VI) was synthesized from vanillin (VII) through the corresponding nitrostyrene (VIII).



The bromination of other phenylethylamines also was investigated. Thus homoveratrylamine (IX) gives β -(3,4-dimethoxy-6-bromophenyl)ethylamine (X), and tyramine (XI) gives 3-bromotyramine (XII) in good yield.



EXPERIMENTAL

β -(3-Methoxy-4-hydroxyphenyl)ethylamine (VI) was prepared through hydrogenation of 3-methoxy-4-hydroxy- ω -nitrostyrene by the Hahn method [19], modified only in the use of a suspension of the nitrostyrene in acetic acid, which permits a considerable increase in the charge. Yield of β -(3-methoxy-4-hydroxyphenyl)ethylamine acid sulfate, 92% M.p. 150-151° (from a mixture of methyl alcohol and ethyl acetate, 1:1).

Yield of base, 97% M.p. 159-160° [19-20]. Hydrochloride, m.p. 213-214° [21].

β -(3-Methoxy-4-hydroxy-5-bromophenyl)ethylamine (I). A) To a solution of 6.24 g of β -(3-methoxy-4-hydroxyphenyl)ethylamine hydrochloride in 40 ml of glacial acetic acid, heated to 70°, was added 7.55 g of dioxan dibromide [22] with stirring, after which the solvent was distilled off in vacuo. The residue was treated with 20 ml of ethyl acetate and left to stand at 0° for 72 hours. The precipitated hydrochloride was filtered off, dissolved in 10 ml of water, and neutralized with aqueous ammonia. The base was separated out and washed with water (30 ml). A colorless, crystalline substance soluble in xylene and bromobenzene on heating. M.p. 169.5-170° (from m-xylene).

Found % C 43.55, 44.15; H 5.21, 5.12; N 5.97, 5.73; Br 32.12, 31.70. $C_9H_{12}O_2NBr$. Calculated % C 43.9; H 4.88; N 5.70; Br 32.55.

The hydrochloride is a colorless, crystalline substance, m.p. 215.5-217° (from a mixture of methyl alcohol and ethyl acetate, 1:1). λ_{max} (water) 285 m μ , log ϵ 3.414.

The picrate is a yellow, crystalline substance, m.p. 194-196° (from methyl alcohol).

B) A three-neck flask provided with a stirrer, reflux condenser, and Soxhlet extractor was charged with 280 ml of an ethereal solution containing 0.45 g of lithium aluminum hydride, 1.5 g of 3-methoxy-4-hydroxy-5-bromo- ω -nitrostyrene [23] being placed in the thimble of the extractor. The reduction was carried out by boiling the ethereal solution for 18 hours, nearly all the nitrostyrene going into solution. Fifty ml of 2 N sulfuric acid was then added. The ether layer was drawn off, and the water layer was neutralized with lithium carbonate to a pH of 6 and heated to boiling, after which the aluminum hydroxide was separated out. To the filtrate 15 ml of a saturated alcoholic solution of picric acid was added, and the mixture was left to stand overnight. The precipitated β -(3-methoxy-4-hydroxy-5-bromophenyl)ethylamine picrate was filtered off and recrystallized twice from water. Yield 1.35 g (51.9%), m.p. 195-196.5°.

Found % C 38.05, 37.62; H 3.2, 2.95; N 11.76, 11.80. $C_{15}H_{15}O_4N_4Br$. Calculated % C 37.95; H 3.16; N 11.78.

The base is a colorless, crystalline substance, m.p. 169-170° (from m-xylene). A mixture test with the base from the preceding experiment gave no melting-point depression.

Found % C 43.90, 44.00; H 4.77, 4.55; N 5.41, 5.37; Br 32.3, 32.33. $C_9H_{12}O_2NBr$. Calculated % C 43.90; H 4.89; N 5.70; Br 32.55.

β -(3-Methoxy-4-hydroxy-6-bromophenyl)ethylamine (V). To a solution of 2 g of β -(3-methoxy-4-hydroxyphenyl)ethylamine acid sulfate in 20 ml of glacial acetic acid was added 1.87 g of dioxan dibromide during 2-3 minutes, the solvent was distilled off in vacuo, and the residue was mixed with 20 ml of ethyl acetate and left to stand at 20° for 72 hours. The precipitated substance was filtered off (m.p. 192-196°) and dissolved in 10 ml of water, and, after neutralization with ammonia, the 6-bromoamine base was isolated in the form of a colorless, crystalline substance. Yield 1.17 g (58.8%), m.p. 187-189°.

Found % C 43.95, 44.04; H 4.52, 4.88; N 5.44, 5.75. $C_9H_{12}O_2NBr$. Calculated % C 43.90; H 4.88; N 5.70.

The hydrochloride is a colorless, crystalline substance, m.p. 232-233° (dec., from a mixture of methyl alcohol and ethyl acetate, 1:1). λ_{\max} (water) 285 m μ , log ϵ 3.714.

Found %: C 38.14; H 4.40; N 4.63. $C_9H_{12}O_2NBr \cdot HCl$. Calculated %: C 38.25; H 4.60; N 4.96.

The picrate is a yellow, crystalline substance, m.p. 205-207° (from aqueous methyl alcohol, 1:1).

β -(3,4-Dimethoxy-6-bromophenyl)ethylamine (X) was prepared from homoveratrylamine hydrochloride and dioxan dibromide by mixing them in equimolar quantities without solvent. Colorless needles, m.p. 137-137.5°.

Found %: C 46.32, 45.9; H 5.50, 5.50; N 5.20. $C_{16}H_{14}O_2NBr$. Calculated %: C 46.2; H 5.39; N 5.39.

The hydrochloride is a colorless, crystalline substance, m.p. 193-194° (from a mixture of methyl alcohol and ethyl acetate, 1:1).

Found %: C 40.20; H 4.80; N 5.05. $C_{16}H_{14}O_2NBr \cdot HCl$. Calculated %: C 40.50; H 5.06; N 4.73.

The picrate is a yellow, crystalline substance, m.p. 196-196.5°.

Found %: C 39.39, 39.28; H 3.80, 3.52; N 11.12, 11.52. $C_{16}H_{14}O_2NBr \cdot C_6H_3O_7N_3$. Calculated %: C 39.30; H 3.48; N 11.45.

3-Bromotyramine (XII) was prepared by mixing equimolar quantities of tyramine hydrochloride and dioxan dibromide without solvent. A colorless, crystalline substance, m.p. 162-164° (from m-xylene).

Found %: N 6.13. $C_8H_{10}ONBr$. Calculated %: N 6.49.

The hydrochloride is a colorless, crystalline substance, m.p. 205.5-207° (from a mixture of methyl alcohol and ethyl acetate, 1:1). λ_{\max} (water) 280 m μ , log ϵ 3.3849.

Found %: N 5.69, 5.54. $C_8H_{10}ONBr \cdot HCl$. Calculated %: N 5.55.

SUMMARY

β -(3-Methoxy-4-hydroxy-5-bromophenyl)ethylamine has been synthesized by the bromination of β -(3-methoxy-4-hydroxyphenyl)ethylamine hydrochloride with dioxan dibromide in an acetic acid medium. The position of the bromine was proved by identification with the substance obtained on reduction of 3-methoxy-4-hydroxy-5-bromo- ω -nitrostyrene with lithium aluminum hydride. It was shown that the bromination of β -(3-methoxy-4-hydroxyphenyl)ethylamine acid sulfate under similar conditions leads to the 6-bromo isomer. β -(3,4-Dimethoxy-6-bromophenyl)ethylamine and 3-bromotyramine, not described earlier, were also obtained.

LITERATURE CITED

- [1] L. V. Volkova, O. N. Tolkachev and N. A. Preobrazhenskii, Proc. Acad. Sci. USSR 102, 521 (1955).
- [2] M. Erne and F. Ramirez, Helv. Chim. Acta. 63, 101 (1951).
- [3] W. M. Whaley and Ch. N. Robinson, J. Org. Ch. 19, 1026 (1954).
- [4] M. Tomita and H. Watanabe, J. Pharm. Soc. Japan. 58, 783 (1938); Ch. A. 33, 2524 (1939).
- [5] Lando, J. Am. Chem. Soc. 27, 641 (1905).
- [6] Th. Zincke and O. Hahn, Lieb. Ann. 329, 1 (1903).
- [7] K. Auwers and O. Müller, Ber. 35, 114 (1902); E. Adler and B. Stenemur, Ber. 89, 291 (1956).
- [8] G. Koerner and B. L. Vanzetti, Mem. acad. Lincei. 8, 749 (1911); Ch. A. 6, 1291 (1912).
- [9] H. G. H. Erdtman, Proc. Roy. Soc. A. 143, 177 (1933).
- [10] H. Kondo, M. Satomi and I. Ikeda, Ann. Rept. Itsuu Lab. 2, 13 (1953); Ch. A. 47, 7519 (1953).
- [11] R. Pschorr, Lieb. Ann. 391, 23 (1912).
- [12] S. Kaufmann, G. Rosenkranz and J. Lopes, J. Am. Chem. Soc. 68, 2733 (1946).

- [13] R. D. Haworth and W. H. Perkin, *J. Chem. Soc.* 127, 1448 (1925).
- [14] J. Rosenkranz and M. Perez, *Ciencia*, 6, 364 (1945).
- [15] Fottcher, *Ber.* 42, 253 (1909).
- [16] E. J. Forbes, *J. Chem. Soc.* 3926 (1955).
- [17] W. Lautsch and G. Piazolo, *Ber.* 73, 317 (1940).
- [18] H. Ishikawa, *J. Jap. Forest Soc.* 35, 121 (1953); *Ch. A.* 48, 6117 (1954).
- [19] G. Hahn and K. Stiehl, *Ber.* 71, 2154 (1938).
- [20] K. Kratzl and G. Billek, *Monatsh.* 83, 1045 (1953).
- [21] F. A. Ramirez and A. Burger, *J. Am. Chem. Soc.* 72, 2781 (1950).
- [22] L. Ia. Ianovskaia, A. P. Terent'ev and L. I. Belen'kii, *J. Gen. Chem.* 22, 1594, 1598 (1952); *24, 1265 (1954).*
- [23] S. P. Makarov, *J. Gen. Chem.* 5, 39 (1935); *J. pr. Ch.* 141, 77 (1934).

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STEREOCHEMICAL INVESTIGATIONS

IV. SCHIFF BASES FROM OPTICALLY ACTIVE α -BENZYLETHYLAMINE

V. M. Potapov and A. P. Terent'ev

In the preceding report [1] we described a series of Schiff bases from optically active α -phenylethylamine (I). The interesting peculiarities of optical rotation, found in this series, occasioned the synthesis and investigation of the optical activity of a second series of Schiff bases. The optically active amine used here was α -benzylethylamine (II), which differs from (I) by the presence of a CH_2 group between the benzene nucleus and the asymmetric center.

We synthesized the racemate of (II) by the reductive amination of phenylacetone (after Leikart). For the synthesis of the initial phenylacetone, methods described in the literature [2, 3] may be used. However, it takes a great deal of time to carry out these syntheses, despite their apparent simplicity. It is much more convenient to prepare the phenylacetone by the catalytic condensation of phenylacetic and acetic acids. This condensation takes place at $410-420^\circ$ over manganous oxide. The yield of phenylacetone in this case reaches 70%.

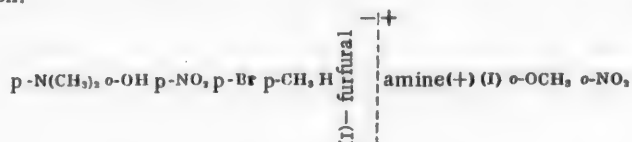
(II) may be resolved into optical antipodes by treatment with D-tartaric acid in alcoholic solution, as described in a number of works [2, 4]. Menthyl hydrogen sulfate, which was used earlier in the preceding works of this series, also proved suitable for resolution. Through menthyl hydrogen sulfate (–) (II) is isolated, while on resolution with D-tartaric acid a diastereomer containing (+) (II) precipitates. Thus a combination of the two reagents makes it possible to obtain both antipodes.

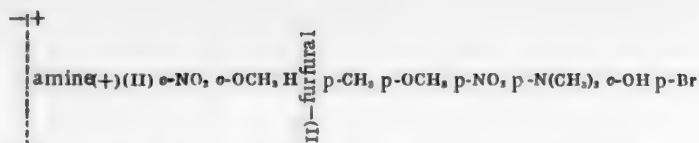
The condensation of optically active (II) with substituted benzaldehydes proceeds smoothly on heating in a water bath without solvent, in benzene, or in methanol. The Schiff base was purified by distillation of recrystallization (the latter was permissible only when the optically pure original amine was used). The constants of the substances obtained are given in the experimental part, whereas data on their optical activity (recalculated for optically pure (+)(II)) are given in Table 1.

The degree and sign of optical rotation of the given series of Schiff bases display peculiarities different from those for the series described in the preceding report. While Schiff bases obtained from (+) (I), as a rule, have the opposite sign of rotation (with the exception of ortho-nitro- and ortho-methoxy-substituted ones), all Schiff bases from (+) (II) without exception retain the (+)-rotation. In this connection, the Schiff bases from (II) appear to be similar to the corresponding α -(β -naphthyl)benzylamine derivatives investigated by Betti [5].

In the (II) series the peculiar character of the o- NO_2 - and o- OCH_3 -derivatives is again found, albeit in a different form from that in the (I) series; here the corresponding Schiff bases are unique, their $[\text{M}]_D$ values being less than the rotation of the Schiff base with unsubstituted benzaldehyde.

Notwithstanding the external difference, a certain similarity in the two series of Schiff bases is found on closer scrutiny. It becomes particularly apparent if the two series of derivatives are arranged in the order of increasing molecular rotation:





The order of the compounds in the two series shows a certain similarity if one series is examined from left to right and the other from right to left; the two series are, as it were, "mirror images." This may be due to the fact that the relative configurations of (+) (I) and (+) (II) are different. The small amount of experimental data, so far accumulated, on the optical activity of Schiff bases is not sufficient to permit any far-reaching conclusions on the causes of the observed peculiarities. However, the following consideration is not devoid of interest.

TABLE 1

Molecular Rotations $[M]_D$ of Schiff Bases from (+)- α -Benzylethylamine $\text{C}_6\text{H}_5\text{CH}_2\text{---CH(CH}_3\text{)---N=CH---C}_6\text{H}_4\text{---X}$

No. of compd.	Substituent X	$[M]_D$ in solvents:				
		benzene	methanol	acetone	dichloroethane	heptane
1	<i>o</i> -NO ₂	200	225	225	198	189
2	<i>o</i> -OCH ₃	374	440	425	401	381
3	H	520	544	538	485	508
4	Furfural (II)	564	722	578	517	578
5	<i>p</i> -CH ₃	567	695	592	512	842
6	<i>p</i> -OCH ₃	683	785	673	610	662
7	<i>p</i> -NO ₂	780	783	730	680	728
8	<i>p</i> -N(CH ₃) ₂	855	855	740	644	891
9	<i>o</i> -OH	880	1135	820	773	895
10	<i>p</i> -Br	1010	1090	987	908	1035

On the basis of the investigation of rotatory dispersion in a series of amines, Lowry and co-workers [6, 7] reached the conclusion that optically active amines may belong to two types. For most amines optical activity is caused primarily by circular dichroism of the absorption band at λ 2300 A, and the formation of this band is due to the free electron pair of the amino nitrogen. For amines of this first type, therefore, the degree of rotation depends strongly on salt formation, in which the electron pair is bound. In the second group of optically active amines the decisive role in the establishment of a definite degree of rotation is played by the dichroism of other absorption bands. In this case salt formation, which affects the electron pair of the amino nitrogen, does not have so much influence on the degree of rotation. Lowry refers α -(β -naphthyl)benzylamine in particular to the second group. At the same time it is known from the work of Betti that Schiff bases of this amine retain the sign of rotation of the original amine.

On the basis of the small difference between the rotations of free (II) and its hydrochloride, we may assume that (II) also should be referred to the second group. In connection with this, (II) behaves like α -(β -naphthyl)benzylamine on conversion to a Schiff base. In the case of (I) salt formation markedly changes the degree of rotation; this amine belongs to the first group, and on conversion to a Schiff base, in contrast to the preceding, the sign of rotation changes.

EXPERIMENTAL

Phenylacetone $\text{C}_6\text{H}_5\text{CH}_2\text{COCH}_3$. From the pasty mass obtained by mixing equal quantities of manganese carbonate and asbestos fiber (with addition of a small amount of waterglass and water) were prepared balls having the size of a pea, which, while still moist, were loaded into a hard-glass tube 2 cm in diameter to form a layer 40 cm long. After drying in a current of warm air the tube was placed in a tubular furnace and the temperature gradually raised to 400° in a slow current of nitrogen; 30 ml of methanol was then admitted, followed at 410-420° by a mixture of 1 part phenylacetic acid and 3 parts glacial acetic acid at a rate of 15-20 drops per minute. Water and a yellowish, oily liquid collected in the receiver. The top layer was drawn off, dried with CaCl_2 , and distilled through a column (dephlegmator). Yield of phenylacetone, up to 70%.

α -Benzylethylamine $C_6H_5CH_2CH(NH_2)CH_3$. The synthesis was carried out by the cited method [2].

B.p. 200-201.5°, n_D^{20} 1.5186.

Literature data: b.p. 204-205°, n_D^{20} 1.5190 [8].*

(+)- α -Benzylethylamine. The resolution of the racemate with D-tartaric acid in alcohol was carried out as described [2]. The pure (+)-amine bitartrate has $[\alpha]_D^{17} + 28.7^\circ$ (water c 8.4).** On decomposition with alkali, followed by distillation, there was isolated (+) (II) $[\alpha]_D^{19} + 36.3^\circ$ (without solvent).

(-)- α -Benzylethylamine was prepared by resolution of the racemate by means of menthyl hydrogen sulfate, as described by us earlier [11]. The diastereomeric salts were separated by repeated recrystallization from water; in this case, in order to avoid large volumes, the more soluble salt might be extracted from the precipitate by boiling water in quantities insufficient to dissolve the precipitate completely. Isolation of the pure diastereomeric salt of the (-) amine requires many crystallizations, and the yield of salt is very small. We stopped with the fifth crystallization, which gave a salt with m.p. 190-191°, having $[\alpha]_D^{20} 51^\circ$ (water c 4); after decomposition with alkali, (-) (II), $[\alpha]_D^{20} - 26^\circ$ (without solvent) was obtained in 30% yield calculated on the basis of the amine used.

o-Nitrobenzal-(-)-benzylethylamine

$o-O_2N-C_6H_4-CH=N-CH(CH_3)-CH_2C_6H_5$. A mixture of 2.89 g of (-) (II), $[\alpha]_D^{20} - 26^\circ$ (optical purity 73.3%),*** 3.23 g of o-nitrobenzaldehyde, and 20 ml of methanol was refluxed for 1.5 hours, the methanol and water were driven off, and the residue was distilled in vacuo. Yield 4.44 g (77%).

B.p. 187-189° (4 mm), d_4^{20} 1.131, n_D^{20} 1.5834, MR_D 79.3; calc. 78.4; $[\alpha]_D^{20} - 54.7^\circ$ (benzene, c 1.4), - 61.5° (methanol, c 1.5), - 61.5° (acetone, c 1.6), - 54.2° (dichloroethane, c 1.1), - 51.7° (heptane, c 1.4).

o-Methoxybenzal-(-)- α -benzylethylamine $o-CH_3O-C_6H_4-CH=N-CH(CH_3)CH_2C_6H_5$ was prepared like the preceding from 2.86 g of (-) (II) and 2.89 g of o-methoxybenzaldehyde in 10 ml of benzene; yield 4.6 g (85.5%).

B.p. 165-166.5° (3 mm), d_4^{20} 1.047, n_D^{20} 1.5782, MR_D 80.3; calc. 78.2. $[\alpha]_D^{20} - 108^\circ$ (benzene, c 2.4), - 127° (methanol, c 2.3), - 123° (acetone, c 2.4), - 116° (dichloroethane, c 2.2), - 110° (heptane, c 1.3).

Found % N 5.48, 5.49. $C_{17}H_{19}ON$. Calculated % N 5.53.

Furfural-(+)- α -benzylethylamine

$C_4H_3O-CH=N-CH(CH_3)-CH_2C_6H_5$ was prepared like the preceding from 2.41 g of (+) (II) (optical purity 100%) and 1.71 g of furfural in 10 ml of benzene; yield 2.9 g (76.3%).

B.p. 133-135° (4 mm), d_4^{20} 1.038, n_D^{20} 1.5640, MR_D 66.9; calc. 64.8. $[\alpha]_D^{20} + 265^\circ$ (benzene, c 1.8), + 339° (methanol, c 1.8), + 272° (acetone, c 1.8), + 243° (dichloroethane, c 1.7), + 272° (heptane, c 1.7).

Found % N 6.89, 6.67. $C_{14}H_{15}ON$. Calculated % N 6.57.

Benzal-(-)- α -benzylethylamine $C_6H_5CH=N-CH(CH_3)CH_2C_6H_5$ was prepared like the preceding from 3.21 g of (-) (II) and 2.52 g of benzaldehyde; yield 3.78 g (72 %).

B.p. 142-144° (3 mm), d_4^{20} 1.002, n_D^{20} 1.5736, MR_D 73.5; calc. 71.9. $[\alpha]_D^{19} - 170^\circ$ (benzene, c 2.2), - 177.5° (methanol, c 4.0), - 176° (acetone, c 3.1), - 158.5° (dichloroethane, c 2.2), - 166° (heptane, c 1.4).

Found % C 86.41, 86.38; H 8.01, 7.93; N 6.17, 6.28. $C_{16}H_{17}N$. Calculated % C 86.06; H 7.63; N 6.27.

*In the cited source [9] n_D^{20} 1.4704 is given. This value is taken from the work of Kenyon and co-workers [10] and is clearly erroneous; it relates to a doubtful substance whose analysis for carbon differs from the theoretical by 0.7%.

**The value $[\alpha]_D^{20} + 21.6^\circ$ refers not to the aqueous solution, as is incorrectly stated in work [2], but to a solution in 1 N hydrochloric acid, for which we obtained $[\alpha]_D^{17} + 21.4^\circ$, whereas Leithe [4] gives the value $[\alpha]_D^{15} + 20.8^\circ$ (1 N hydrochloric acid, c 7.8).

***This batch of (-) (II) was used also for the preparation of other Schiff bases, besides salicylal-p-bromobenzal-, p-dimethylaminobenzal- and furfural derivatives.

p-Toluyal-(-)- α -benzylethylamine

$p\text{-CH}_3\text{-C}_6\text{H}_4\text{CH}=\text{N-CH}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_5$ was prepared like the preceding from 3.8 g of (-) (II) and 3.16 ml of p-tolualdehyde; yield 3.45 g (52%).

B.p. 158-159° (3 mm), d_4^{20} 0.9897, n_D^{20} 1.5712, M_{rD} 78.8; calc. 76.5. $[\alpha]_D^{19}$ -176° (benzene, c 1.9) -217° (methanol, c 1.9) -183.5° (acetone, c 2.2), -159° (dichloroethane, c 2.2), -262° (heptane, c 1.1).

Found % N 5.80, 6.03. $\text{C}_{17}\text{H}_{19}\text{N}$. Calculated % N 5.90.

p-Methoxybenzal-(-)- α -benzylethylamine

$p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}=\text{N-CH}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_5$ was prepared like the preceding from 5.07 g of (-) (II) and 5.10 g of anisaldehyde; yield 7.29 g (72%).

B.p. 167-170° (3 mm), d_4^{20} 1.047, n_D^{20} 1.5818, M_{rD} 80.7; calc. 78.2. $[\alpha]_D^{19}$ -197° (benzene, c 1.8), -227° (methanol, c 2.3), -194° (acetone, c 2.0), -176° (dichloroethane, c 1.6), -191° (heptane, c 1.7).

Found % N 6.04, 6.16. $\text{C}_{17}\text{H}_{19}\text{ON}$. Calculated % N 5.53.

p-Nitrobenzal-(-)- α -benzylethylamine

$p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}=\text{N-CH}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_5$ was prepared like the preceding from 2.46 g of (-) (II) and 2.75 g of p-nitrobenzaldehyde in 30 ml of methanol. After the methanol was evaporated, the reaction product was isolated in solid form, m.p. 67-72° (unsharp because the substance was not optically pure).

$[\alpha]_D^{19}$ -213° (benzene, c 2.3), -214° (methanol, c 2.1), -200° (acetone, c 2.4), -186° (dichloroethane, c 1.5), -199° (heptane, c 1.8).

Found % N 10.26, 10.11. $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$. Calculated % N 10.44.

p-Dimethylaminobenzal-(+)- α -benzylethylamine

$p\text{-(CH}_3)_2\text{N-C}_6\text{H}_4\text{-CH}=\text{N-CH}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_5$. Prepared like the preceding from 5.1 g of (+) (II), $[\alpha]_D^{20}$ +19.2° (optical purity 53%), and 5.7 g of p-dimethylaminobenzaldehyde in 30 ml of benzene; yield 7.6 g (74%).

B.p. 216-219° (5 mm), m.p. 48-53°. $[\alpha]_D^{18}$ +170° (benzene, c 2.1), +170° (methanol, c 1.9), +147° (acetone, c 2.3), +128° (dichloroethane, c 1.4), +177° (heptane, c 2.0).

Found % N 10.56, 10.66. $\text{C}_{18}\text{H}_{22}\text{N}_2$. Calculated % N 10.52.

Salicylal-(+)- α -benzylethylamine

$o\text{-HOC}_6\text{H}_4\text{-CH}=\text{N-CH}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_5$ was prepared like the preceding from 2.8 g of (+) (II) (optical purity 75%) and 2.55 g of salicylaldehyde in 10 ml of methanol; yield 2.45 g (49.5%).

B.p. 164-168° (2 mm), m.p. 47-54° (unsharp owing to incomplete optical purity). $[\alpha]_D^{20}$ +269° (benzene, c 2.1), +347° (methanol, c 2.4), +252° (acetone, c 1.9), +237° (dichloroethane, c 2.5), +274° (heptane, c 1.6).

Found % N 5.95, 6.05. $\text{C}_{16}\text{H}_{17}\text{ON}$. Calculated % N 5.85.

p-Bromobenzal-(+)- α -benzylethylamine

$p\text{-BrC}_6\text{H}_4\text{CH}=\text{N-CH}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_5$ was prepared like the preceding from 0.59 g of (+) (II) (optical purity 100%) and 0.80 g of p-bromobenzaldehyde in 20 ml of methanol; it was purified by recrystallization from aqueous alcohol; yield nearly quantitative, m.p. 65°.

$[\alpha]_D^{20}$ +243° (benzene, c 1.6), +264° (methanol, c 1.3), +240° (acetone, c 1.8) +221° (dichloroethane, c 1.6), +252° (heptane, c 1.3).

Found % N 4.40, 4.57. $\text{C}_{16}\text{H}_{16}\text{NBr}$. Calculated % N 4.64.

SUMMARY

1. α -Benzylethylamine has been resolved into optical antipodes by means of (-) menthyl hydrogen sulfate.
2. Schiff bases have been prepared from optically active α -benzylethylamine and aromatic aldehydes. Their optical activity in benzene, methanol, acetone, dichloroethane, and heptane has been determined.

LITERATURE CITED

- [1] A. P. Terent'ev and V. M. Potapov, J. Gen. Chem. 28, 1161 (1958). *
- [2] O. Iu. Magidson and G. A. Garkusha, J. Gen. Chem. 11, 339 (1941).
- [3] B. R. Bobranskii and Ia. V. Drabik, J. Appl. Chem. 14, 410 (1941).
- [4] W. Leither, Ber. 65, 660 (1932).
- [5] M. Betti, Trans. Faraday Soc. 26, 337 (1930).
- [6] T. M. Lowry and W. C. G. Baldwin, Proc. Roy. Soc. 162 A, 204 (1937); Zbl. II, 1566 (1938).
- [7] W. C. G. Baldwin, Proc. Roy. Soc. 162 A, 215 (1937); Zbl. II, 1567 (1938).
- [8] J. Hald and J. Gad, Dansk Tidsskr. Farmac. 12, 97 (1938); Zbl. II, 1275 (1938).
- [9] Dictionary of Org. Comp. III, 426 (1949). **
- [10] J. Kenyon, H. Phillips and V. P. Pittman, J. Chem. Soc. 1072 (1935).
- [11] A. P. Terent'ev and V. M. Potapov, J. Gen. Chem. 27, 1092 (1957). *

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INVESTIGATIONS IN THE FIELD OF ORGANOCYCLOSILOXANES

IV. REACTIVITY OF ORGANOCYCLOSILOXANES IN DEPENDENCE ON THE NUMBER OF LINKS IN THE CYCLE

N. N. Sokolov

There is practically no information in the literature on the reactivity of cyclic organosilicon compounds. The mechanism of polymerization of organocyclosiloxanes by acid [1, 2] and basic [2-4] catalysts was studied only in application to reactions of rearrangement of linear and cyclic hydrolysis products of the monomers. A qualitative conclusion has been reached, on the more rapid polymerization of hexamethylcyclotrisiloxane in comparison with octamethylcyclotetrasiloxane. This effect is explained by the strain in the trimer ring [1].

The small amount of trimer in the hydrolysis products of dimethyldichlorosilane [5] also indicates the strain in this ring in comparison with higher ones. This conclusion is contradicted by the presence of a large amount of trimers in the hydrolysis products of diethyldichlorosilane [6] and the products of thermal re-forming of polydimethylsiloxanes [5].

A report [7] on the varying reactivity of dibutoxycyclosiloxanes should be noted: the trimer was 92% hydrolyzed by boiling water after 72 hours and the tetramer, 39%; after 48 hours the pentamer was 5% hydrolyzed and the hexamer, 3%. An open-chain compound, hexabutoxydisilane, was 5% hydrolyzed after 72 hours.

For the experiments we took cyclic compounds having a varying number of Si-O links in the ring and various radicals (substituents) attached to the silicon.

Since hydrogen in compounds containing a Si-H bond reacts with alkalis, concentrated sulfuric acid (d 1.83) was used as polymerization catalyst, in the amount of 0.4 g for each 1/30 mole of the cyclic compound.

The rate of polymerization of cyclic compounds containing a Si-H bond, as preliminary experiments showed, was very high in comparison with that of cyclic compounds containing alkyl radicals and was moderated by using solvents. As in the case of polymerization of organic monomers, the polymerization rate, characterized by the change in the relative viscosity (η) of a 10% solution in benzene, increases as the dipole moment of the solvent increases (Table 1).

In the experiments benzene was used as a solvent. At a 50% concentration of the compounds being investigated the reaction rate is still quite high and can be measured, whereas at 30% concentration the reaction practically does not occur. The relative viscosity of the solution proved to be a linear function of the percentage (up to 4%) of catalyst for constant reaction time.

It should be noted that after a certain degree of polymerization ($\eta = 3-5$) is attained, a decrease of viscosity is observed in all cases. This effect is due to cessation of chain growth and to destruction of the already-formed polymer under the influence of the catalyst, as a result of which equilibrium is attained in the polymerized system. The given process takes place especially vigorously in solvents. On determining the viscosity of a 10% solution after the viscosity maximum is reached in a viscometer, a gradual decrease of viscosity is observed. In Fig. 1 are given the results of determination of η for a solution of 1 g of dimethylpolysiloxane rubber in 49 g of toluene or chlorobenzene in the presence of 4% of sulfuric acid. Under the same conditions, but without catalyst, no decrease of viscosity is observed.

TABLE 1

Effect of the Dipole Moment of the Solvent on the Rate of Polymerization of Triethylcyclotrisiloxane

Solvent	$\mu \cdot 10^{18}$	η after 20 minutes
Benzene	0	1.73
n-Heptane	0	1.85
Carbon tetrachloride	0	1.70
Toluene	0.4	2.07
Chlorobenzene	1.7	2.76
Nitrobenzene	4.0	5.0

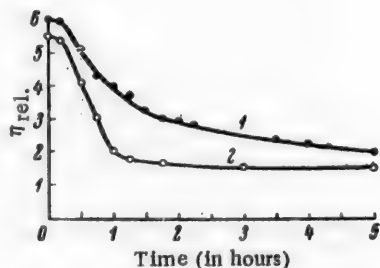


Fig. 1. Effect of solvents on the de-polymerization of polydimethylsiloxane.
1) Toluene; 2) chlorobenzene.

The trimers all differ sharply in reactivity. Trimethylcyclotrisiloxane polymerizes rapidly (with decomposition), hexamethylcyclotrisiloxane polymerizes 351 times as quickly as octamethylcyclotetrasiloxane, etc.

The decisive role in determining polymerizability is played by the size of the radicals (substituents) attached to the silicon. As the radical becomes larger, the polymerization rate decreases. Thus the ratio of the polymerization times of tetramers with the substituents $\text{CH}_3\text{-H}$, $\text{C}_2\text{H}_5\text{-H}$, $\text{CH}_3\text{-CH}_3$, $\text{C}_2\text{H}_5\text{-C}_2\text{H}_5$ is equal to 1:11:586:10,286.

The effect of ring size on reactivity has been confirmed by us in the case of the cyclic series $[\text{CH}_3\text{SiO}]_{3-6}$.

The oxidizability and reducing action of silanes are well known. Reactions of replacement of hydrogen in the Si-H bond in organo-substituted silanes also have been studied [8, 9].

In the study of the reactions of methylcyclosiloxanes with various reagents we found that trimethylcyclotrisiloxane is exceptionally nucleophilic. In contrast to higher cyclic compounds of the given series the trimer reduces Fe^{+++} to Fe^{++} , Cu^{++} to Cu , and Ag^+ to Ag within a few minutes. Conc. HNO_3 is reduced by the trimer with evolution of NO_2 and formation of SiO_2 within 1 minute; in the case of the tetramer this process takes 40 minutes; in that of the pentamer, ~3 hours; in that of the hexamer, 4-15 hours. It is generally known that conc. H_2SO_4 does not react even with silanes, but acts as a catalyst in the polymerization of organocyclosiloxanes containing a Si-H bond. However, it was found that trimethylcyclotrisiloxane vigorously reduces sulfuric acid with rapid evolution of SO_2 , which is not produced by higher cyclic compounds of this series or open-chain compounds under the same conditions.

*We adhere to the established terminology, according to which the Si-O link is a member of the ring in organocyclosiloxanes.

In Figs. 2 and 3 is shown the kinetics of polymerization of organocyclosiloxanes containing a Si-H bond and without this bond (hexamethylcyclotrisiloxane measured in benzene), respectively.

In order to compare the rates of polymerization with and without solvent, triethylcyclotrisiloxane and tetraethylcyclotetrasiloxane were polymerized without benzene. It was found that 1:1 dilution with benzene increases time of the attainment of $\eta = 2.0$ sixtyfold. Proceeding from this transition coefficient, the time τ (in seconds) of polymerization of organocyclosiloxanes to $\eta = 2.0$, τ_{corr} , corrected by means of the coefficient, and the time τ_0 , which is assumed to be equal to 1 for tetramethylcyclotetrasiloxane, are given in Table 2.

It follows from the experimental results, that as the number of links in rings with identical radicals increases, the time of polymerization to $\eta = 2$ increases. However, this increase is slight and apparently tends toward some limit. Thus, in the series $[\text{CH}_3\text{SiO}]_{4-6}$ the ratio of the polymerization

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H

time τ_0 of the pentamer to that of the tetramer is 1.47, whereas the corresponding ratio for the hexamer and pentamer is 1.22. In the series $[(\text{CH}_3)_2\text{SiO}]_{4-6}$ the corresponding ratio for the pentamer and tetramer is 2.36, and that for the hexamer and pentamer is 1.86.*

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TABLE 2

Rate of Polymerization of Organocyclosiloxanes

Cyclosiloxanes	Formula	Polymerization time (in sec)		τ_0
		τ in expt.	τ_{corr}	
Trimethylcyclotrisiloxane	$\left[\begin{array}{c} \text{CH}_3\text{SiO} \\ \\ \text{H} \end{array} \right]_3$	< 1 with dec.	≤ 1	≤ 1
Tetramethylcyclotetrasiloxane	$\left[\begin{array}{c} \text{CH}_3\text{SiO} \\ \\ \text{H} \end{array} \right]_4$	252	4.2	1
Pentamethylcyclopentasiloxane	$\left[\begin{array}{c} \text{CH}_3\text{SiO} \\ \\ \text{H} \end{array} \right]_5$	374	6.2	1.47
Hexamethylcyclohexasiloxane	$\left[\begin{array}{c} \text{CH}_3\text{SiO} \\ \\ \text{H} \end{array} \right]_6$	456	7.6	1.81
Triethylcyclotrisiloxane	$\left[\begin{array}{c} \text{C}_2\text{H}_5\text{SiO} \\ \\ \text{H} \end{array} \right]_3$	758	12.6	3.0
Tetraethylcyclotetrasiloxane	$\left[\begin{array}{c} \text{C}_2\text{H}_5\text{SiO} \\ \\ \text{H} \end{array} \right]_4$	2760	46	11.0
Pentaethylcyclopentasiloxane	$\left[\begin{array}{c} \text{C}_2\text{H}_5\text{SiO} \\ \\ \text{H} \end{array} \right]_5$	4500	75	17.8
Hexamethylcyclotrisiloxane	$[(\text{CH}_3)_2\text{SiO}]_3$	420	7	1.66
Octamethylcyclotetrasiloxane	$[(\text{CH}_3)_2\text{SiO}]_4$	2460	2460	586
Decamethylcyclopentasiloxane	$[(\text{CH}_3)_2\text{SiO}]_5$	5820	5820	1386
Dodecamethylcyclohexasiloxane	$[(\text{CH}_3)_2\text{SiO}]_6$	10800	10800	2570
Hexaethylcyclotrisiloxane	$[(\text{C}_2\text{H}_5)_2\text{SiO}]_3$	23400	23400	5570
Octaethylcyclotetrasiloxane	$[(\text{C}_2\text{H}_5)_2\text{SiO}]_4$	43200	43200	10286

Turning to the experience of organic chemistry, we find that the Baeyer-Sachse-Mohr theory made it possible to relate ring strain in cyclic compounds generally to their reactivity. Carothers further concluded that the stability of cyclic compounds depends on the size of the ring, increasing as the latter increases [10]. Correlations between ring size and reactivity were found for cycloalkane derivatives [11]. On the basis of the ability of cycloolefins to form complexes with silver, it was established [12] that the degree of strain, with regard to which cyclopentane \geq cycloheptane $>$ cyclohexane, corresponds to the reactivity; in this case, the electron-donor properties of the cyclic compounds are enhanced as the strain increases. Strepikheev and Skuratov [13] determined the heats of combustion of certain lactams, as well as their strain, and found that a high degree of ring strain corresponds to a high rate of polymerization. They noted that the reactivity of heterocyclic compounds of the same ring structure depends on the structure of the substituents.

Korshak [14], on generalizing the voluminous experimental data, reached the conclusion that the polymerizability of heterocyclic compounds accords in the main with the strain theory. Three-membered rings polymerize most readily. The screening effect of substituents is very important.

In organocyclosiloxanes a great degree of strain in the trimers must be assumed. Actually a Si-O-Si bond angle of $160 \pm 15^\circ$ was found in open-chain polymethylsiloxanes [15], whereas the O-Si-O bond angle is near $109^\circ 28'$. The oxygen bond angle in polyethylsiloxanes was found to be 168° [16]. In disiloxane $\text{H}_3\text{SiOSiH}_3$ this angle is assumed to be almost linear (180°) [17]. Flory [18] thinks that the most probable value of the oxygen bond angle is 145° . From these data it must be concluded that considerable strain is present in the cyclic trimers. It was found [19] that hexamethylcyclotrisiloxane has a strained planar structure, while the strain in octamethylcyclotetrasiloxane is mitigated by the nonplanar configuration of the ring. Obviously a nonplanar configuration must be assumed also for the higher organocyclosiloxanes.

EXPERIMENTAL

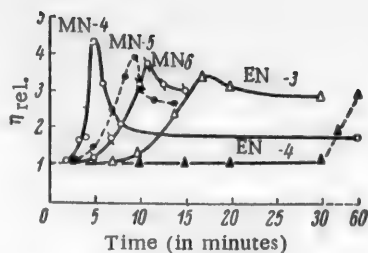


Fig. 2. Kinetics of polymerization of methyl- and ethylcyclotrisiloxanes containing a Si-H bond.

MN-4) Tetramethylcyclotetrasiloxane; MN-5) pentamethylcyclopentasiloxane; MN-6) hexamethylcyclohexasiloxane; EN-3) triethylcyclotrisiloxane; EN-4) tetraethylcyclotetrasiloxane.

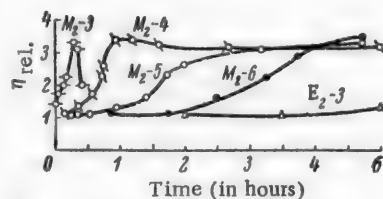


Fig. 3. Kinetics of polymerization of dimethyl- and diethylcyclotrisiloxanes.

M₂-3) Hexamethylcyclotrisiloxane; M₂-4) octamethylcyclotetrasiloxane; M₂-5) decamethylcyclopentasiloxane; M₂-6) dodecamethylcyclohexasiloxane; E₂-3) hexaethylcyclotrisiloxane.

For control, experiments on the polymerization of certain organocyclosiloxanes were performed with the same quantity of catalyst. It was found that the variation in the amount of catalyst, resulting from its calculation on the basis of the molecular weight of one or another organocyclosiloxane, cannot have any substantial effect on the results of the experiments. Thus η for tetraethylcyclotetrasiloxane with 0.27 g of sulfuric acid after 17 minutes was equal to 1.04, while η for triethylcyclotrisiloxane with the same quantity of sulfuric acid after 17 minutes was 3.4; η for decamethylcyclopentasiloxane with 0.81 g of sulfuric acid after 1 hour was 1.6, while η for octamethylcyclotetrasiloxane with the same amount of catalyst after the same time reached 3.4.

To compare the polymerization rates with and without solvent, 20 g of tetraethylcyclotetrasiloxane with 0.816 g of catalyst was polymerized without benzene, $\eta = 2.0$ being reached after 45 seconds. In the experiment with benzene the same viscosity was reached after 46 minutes. In the case of triethylcyclotrisiloxane $\eta = 2.0$ was obtained after 11 seconds and 12 minutes 32 seconds, respectively. From this a transition coefficient of 60 (within the limits of experimental error) was derived.

The effect of solvents on the polymerization rate was studied in the case of triethylcyclotrisiloxane. Five g of the latter (+ 0.27 g of sulfuric acid) and 0.064 mole of solvent were taken. The duration of the experiment at 20° was 20 minutes, after which the entire reaction solution was diluted with benzene to 10% concentration and the viscosity was determined.

The polymerization experiments were performed in a 90 ml, round-bottom flask provided with necks for a reflux condenser and a mercury-seal stirrer, for a thermometer, and for sampling. The stirrer was driven by a constant-current motor with a reducing gear and had a constant rate of 315 rpm. The lower end of the stirrer was set at a fixed distance of 1 mm from the bottom of the flask. The temperature was maintained at $21 \pm 0.1^\circ$ by a water thermostat. Organocyclosiloxanes not containing a Si-H bond were taken in 20 g quantities; sulfuric acid was taken at a rate of 0.4 g per 1/30 mole of the substance being polymerized. Thus, for instance, 0.81 g of sulfuric acid was taken for octamethylcyclotetrasiloxane (M_{296} , $1/30 M = 9.9$). Samples were weighed into a prepared tare and immediately dissolved in about half the amount of benzene in order to arrest polymerization. This operation took not more than 1 minute. Then the required weight of benzene was added.

Organocyclosiloxanes containing a Si-H bond were taken in the amount of 5 g + 5 g of benzene. The catalyst was introduced in the amount previously calculated for 5 g of the organocyclosiloxane. Because of the rapid course of the reaction with cyclic compounds of this group, no samples were taken during the reaction. Each experiment was performed separately during a set time. At the end of the set time 40 g of benzene was added all at once to the reaction mixture in the flask, with the stirrer running. This stopped the reaction, and a solution ready for viscosity measurement was obtained.

All experiments were performed under strictly identical conditions, since the polymerization rate, according to preliminary data, is considerably affected by the experimental conditions — the shape of the vessel, stirring rate, volume of the liquid phase, etc.

The procedure and apparatus adopted, as control experiments showed, provides good reproducibility of results.

SUMMARY

1. The dependence of the reactivity of organocyclosiloxanes on ring size has been elucidated on the basis of a study of polymerization reactions and reducing action.
2. It has been established that as the number of links in the rings, and also the number of substituents attached to the silicon, increases, the polymerizability decreases.
3. Cyclic trimers display enhanced reactivity, trimethylcyclotrisiloxane in particular; the hydrogen of the Si-H bond in the latter has pronounced electron-donor properties.

LITERATURE CITED

- [1] D. W. Scott, J. Am. Chem. Soc. 68, 2294 (1946).
- [2] S. W. Kantor, W. T. Grubb and R. C. Osthoff, J. Am. Chem. Soc. 76, 5190 (1954).
- [3] D. T. Hurd, R. C. Osthoff and M. L. Corrin, J. Am. Chem. Soc. 76, 249 (1954).
- [4] W. T. Grubb and R. C. Osthoff, J. Am. Chem. Soc. 77, 1405 (1955).
- [5] W. J. Patnode and D. F. Wilcock, J. Am. Chem. Soc. 68, 358 (1946).
- [6] D. T. Hurd and R. C. Osthoff, J. Am. Chem. Soc. 75, 234 (1953).
- [7] R. K. Iler, Ind. Eng. Ch. 39, 1384 (1947).
- [8] F. R. Price, J. Am. Chem. Soc. 69, 2600 (1947).
- [9] B. N. Dolgov, N. P. Kharitonov and M. G. Voronkov, J. Gen. Chem. 24, 678 (1954).*
- [10] W. H. Carothers, G. L. Dorough and F. J. van Natta, J. Am. Chem. Soc. 54, 761 (1932).
- [11] H. C. Brown, J. H. Brewster and H. Shechter, J. Am. Chem. Soc. 76, 467 (1954).
- [12] J. G. Traynham and M. F. Sehnert, J. Am. Chem. Soc. 78, 4024 (1956).
- [13] A. A. Strepikheev and S. M. Skuratov, Proc. Acad. Sci. USSR 102, 105 (1955).
- [14] V. V. Korshak, General Methods of Synthesis of High-Molecular Compounds, Acad. Sci. USSR 102 (1953).**
- [15] R. O. Sauer and D. J. Mead, J. Am. Chem. Soc. 68, 1794 (1946).
- [16] K. A. Andrianov, Organosilicon Compounds, State Chem. Press, 23 (1955). **
- [17] R. C. Lord, D. W. Robinson and W. C. Shumb, J. Am. Chem. Soc. 78, 1327 (1956).
- [18] P. J. Flory, Principles of Polymer chemistry, N. Y. 102, 420 (1953).
- [19] R. C. Osthoff, W. T. Grubb and Ch. Burkhard, J. Am. Chem. Soc. 75, 2227 (1953).

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**In Russian.

INVESTIGATIONS IN THE NAPHTHALENE SERIES

XVIII. ON THE KINETICS OF INTERACTION OF β -NAPHTHOL WITH AQUEOUS SOLUTIONS OF AMMONIA AND AMMONIUM SULFITE*

V. V. Kozlov and I. K. Veselovskaia

The amination of naphthols by aqueous solutions of ammonia in the presence of sulfites is of great practical importance in the preparation of naphthylamines. The chemism of this interaction is explained by the scheme proposed by N. N. Vorozhtsov [1] and is interpreted by us in the following form:

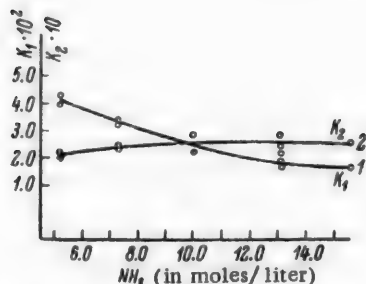
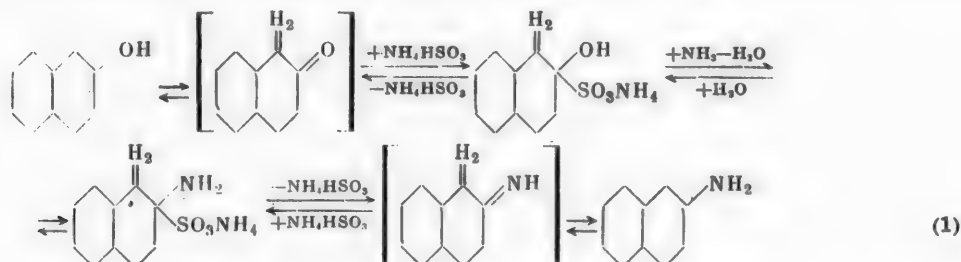


Fig. 1. Dependence of the rate constant for the amination of β -naphthol on the ammonia concentration.

Naphthol may react with sulfites both in the keto form, in which it has not yet been possible to isolate it [2], and in the enol form, which gives an addition product corresponding to the keto form. The kinetic aspect of this process has not been described, either.

Below we set forth the results of a study of the kinetics of interaction of β -naphthol (m.p. 122°) with aqueous ammonia in the presence of ammonium sulfite.

The aqueous ammonia solution was prepared by saturating distilled water with ammonia gas (the concentration of the solutions was determined by titration with 0.5 N sulfuric acid).

Crystalline ammonium sulfite was prepared by saturating a 35% aqueous ammonia solution with sulfur dioxide gas. The $(\text{NH}_4)_2\text{SO}_3$ concentration was determined iodometrically before each experiment.

The amination was carried out in a rotary steel autoclave of 245 ml capacity which was wrapped in asbestos and uniformly heated by a gas-burner flame. The temperature within the autoclave did not vary more than $\pm 0.5^\circ$ during the experiment. The heating of the contents of the autoclave to 150-180° lasted 15-16 minutes. At the end of the stated time the autoclave was cooled with cold water to 70°. After 30 minutes the completely cooled autoclave was opened for emptying.

* For paper XVII see: JGC 27, 3041 (1957) [See C.B. Translation].

TABLE 1

Dependence of the Reaction Rate on the Ammonia Concentration

Concentration of NH_4 (in %)		27.5	24.53	18.3	13.27	9.22
C_a		15.58	13.10	9.93	7.34	5.21
C_s		0.350	0.350	0.353	0.349	0.350
a (in %)		70.80	61.0	55.1	51.0	38.1
Temperature		159.8°	160.2°	160.0°	159.8°	159.7°
$K_1 \cdot 10^3$		1.64	2.17	2.22	3.22	4.23
$K_2 \cdot 10$		2.55	2.84	2.21	2.36	2.21
						0.380
						41.1
						160.0°
						3.91
						2.04

Note: Experimental conditions: 5.505 g of β -naphthol, 6.00 g of $(\text{NH}_4)_2\text{SO}_3$, 100 ml of ammonia (9-27%), 160°, 60 minutes.

The contents of the autoclave were quantitatively transferred with the aid of water to a vessel, and the precipitate which was present in the mixture was filtered off and washed with 5% sodium hydroxide solution until the wash waters ceased to give a test for β -naphthol. The unreacted β -naphthol in the combined solution of mother liquor and wash waters was determined by adding 50 ml of the solution to a 0.1 N solution of a benzenediazonium salt in a soda medium. The amount of ammonia in the experiments corresponded to 13-40 moles per mole of β -naphthol, which assured a practically constant ammonia concentration and the presence of β -naphthol in the solution during the high-temperature reaction.

The rate constant of the reaction of β -naphthol with ammonia in the presence of ammonium sulfite was originally calculated according to Eq. (2), where

$$K_1 = \frac{2.303}{t \cdot C_s} \cdot \lg \frac{100}{a}, \quad (2)$$

t is the reaction time in minutes, C_s is the ammonium sulfite concentration (in moles/liter), and a is the quantity of unreacted β -naphthol (in % of that taken).

This equation is derived from the hypothesis that the reaction rate is directly proportional to the β -naphthol and sulfite concentrations and does not depend on the ammonia concentration. From the experimental results of the study of the interaction of β -naphthol, ammonium sulfite, and ammonia of various concentrations, given in Table 1 and Fig. 1 (Curve 1), the variation of the reaction rate constant may be determined in the range from $1.64 \cdot 10^{-2}$ to $4.07 \cdot 10^{-2}$ moles/liter/minute.

Assuming that the rate of the reaction of β -naphthol with ammonia in the presence of ammonium sulfite is directly proportional not to the concentration of the latter, but to that of ammonium bisulfite as a consequence of dissociation according to scheme (3), we made the appropriate calculations.



On the basis of the relation

$$\frac{[\text{NH}_4\text{HSO}_3][\text{NH}_4\text{OH}]}{[(\text{NH}_4)_2\text{SO}_3]} = K_{\text{hydr.}} \quad (4)$$

the ammonium bisulfite concentration may be expressed by the equation

$$C_{bs} = K_{\text{hydr.}} \frac{C_s}{C_a}, \quad (5)$$

where: C_{bs} is the ammonium bisulfite concentration, C_s is the ammonium sulfite concentration, and C_a is the ammonia concentration.

TABLE 2

Dependence of the Reaction Rate Constant on the β -Naphthol Concentration

$C_{10}H_7OH$ (in g)	2.736		5.472		8.208	
α (in %)	64.2	61.4	69.4	65.4	66.9	61.7
Temperature	160.0°	160.0°	160.0°	160.0°	160.2°	160.4°
$K_2 \cdot 10$	2.52	2.79	2.15	2.45	2.29	2.75

Note: Experimental conditions: 100 ml of 24.2% ammonia, 6.30 g of $(NH_4)_2SO_3$, 160°, 60 minutes.

TABLE 3

Dependence of the Reaction Rate Constant on the Amount of Ammonium Sulfite

$(NH_4)_2SO_3$ (in g)	2.84		3.88		8.14	
C_s	0.163		0.223		0.463	
C_a	13.20		12.44		12.44	
α (in %)	85.0	85.0	74.6	73.4	52.8	
Temperature	160.2°	159.9°	159.6°	159.6°	160.5°	
$K_2 \cdot 10$	2.20	2.20	2.72	2.87	2.82	

Note: Experimental conditions: 5.505 g of β -naphthol, 100 ml of 24.3% ammonia, 160°, 60 minutes.

TABLE 4

Dependence of the Reaction Rate Constant on Time

Duration of experiment (in minutes)	90		120		150	
C_s	0.360	0.380	0.360	0.297	0.352	0.285
α (in %)	49.0	54.5	38.7	54.5	36.7	51.1
Temperature	159.8°	160.7°	160.0°	159.9°	160.1°	160.0°
$K_2 \cdot 10$	2.88	2.33	2.88	2.23	2.49	2.08
Naphthylamine (in %)	40.6		—		58.8	

Note: Experimental conditions: 5.505 g of β -naphthol, 100 ml of 24.5% ammonia, 160°.

The practical invariance of the rate constant (K_2), calculated according to Eq. (6)

$$K_2 = \frac{2.303 \cdot C_a}{t \cdot c_s} \lg \frac{100}{a} \quad (6)$$

and given in Table 1 and Fig. 1 (Curve 2), shows that the reaction rate actually is directly proportional to the bisulfite concentration.

From the data of Tables 2-4 on determination of the dependence of the rate constant on the β -naphthol

TABLE 5

Dependence of the Reaction Rate Constant on Temperature

Temperature	150.4	149.4	150.0	159.6	160.2	160.0	169.6	170.0	170.2	180.7	180.2
C_s	0.380	0.380	0.380	0.380	0.380	0.380	0.361	0.204	0.200	0.361	0.300
a (in %)	80.1	79.5	82.8	65.4	61.0	65.4	44.8	47.7	47.7	34.7	43.6
K_2 exptl.	0.128	0.132	0.109	0.245	0.284	0.245	0.485	0.532	0.538	0.640	0.607
K_2 exptl. av.		0.120		0.247				0.518		0.623	
K_2 calcd.		0.118		0.249				0.512		1.018	

Note: Experimental conditions: 5.505 g of β -naphthol, 6.00 g of $(NH_4)_2SO_3$, 100 ml of 24.5% ammonia, 60 minutes.

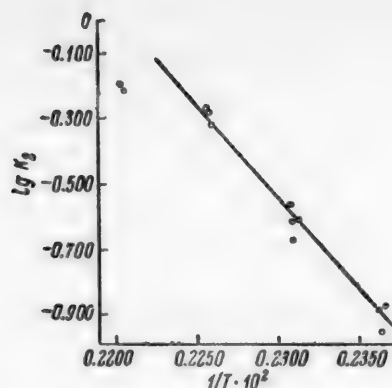


Fig. 2. Dependence of the rate constant of the amination of β -naphthol on temperature.

concentration, the amount of ammonium sulfite taken, and the duration of the experiment, it can be established that the value of the reaction rate constant (K_2), calculated according to Eq. (6), is practically invariant. (The variation in the value of the reaction rate constant in dependence on the amount of the charge in the autoclave, as calculations showed, lies within acceptable limits).

In a work on the amination of 1,5- and 1,4-naphthol-sulfonic acids Cowdrey [3] gives a scheme in which he assumes that the HSO_3^- ion takes part in the reaction. Furthermore, in the corresponding calculations he does not take into account the degree of dissociation of the different sulfites, but states that the rate of the amination reaction depends on the concentration of SO_3^{2-} ions and bound NH_4 , thereby making an obvious error.

The reaction rate constants at various temperatures are given in Table 5.

The dependence of $\lg K_2$ on the inverse temperature is shown in the form of a straight line in Fig. 2. Experimental values of $\lg K_2$, in accordance with the Arrhenius equation, fit the straight line well.

From the data of Table 5 the calculated activation energy of the reaction of β -naphthol with aqueous ammonia in the presence of ammonium sulfite is equal to 27,300 cal/mole.

The dependence of the reaction rate constant on temperature may be represented by the equation:

$$\lg K_2 = 13.219 - \frac{5984.8}{T} \pm 0.008. \quad (7)$$

Values of the constant, calculated by this equation, are given in the last line of Table 5 and agree fully with the experimentally determined constants. Constants found

in experiments at 180° are somewhat diminished owing to a change in the sulfite concentration, caused by slight corrosion observed in the autoclave. The cause of the latter was an increase in the NH_4HSO_3 concentration, due to the great degree of dissociation of $(\text{NH}_4)_2\text{SO}_3$, occurring at high temperature with appreciable transition of ammonia to the gas phase. As is evident from the data of Table 1, an increase in the ammonia concentration leads to a decrease in the amount of naphthol entering into the reaction, probably owing to a decrease in the dissociation of ammonium sulfite according to scheme (3).

The completeness and character of the hydrolysis of the different sulfites, and hence the effect of hydrolysis on the completeness of the amination of naphthol, are evident from the following results, which were obtained by us in the reaction of aqueous ammonia and β -naphthol for 6 hours at 180°; in the presence of ammonium sulfite the percentage of conversion was 94, in that of sodium ammonium sulfite it was 88, and in that of sodium sulfite it was 40.

Thus the data set forth fully confirm reaction scheme (1) for amination.

We shall return to the doubts, expressed by Cowdrey [4] regarding the need for formation of an addition product through preliminary ketonization, in a separate paper.

The rate of the entire amination process is determined by the rate of its first phase, i.e., the rate of the reaction of β -naphthol with bisulfite (NH_4HSO_3 or NaHSO_3). The addition product of scheme (1) is extremely reactive, and therefore it reacts further with ammonia to form naphthylamine at a rapid rate, greatly exceeding the rate of its formation. The rate of conversion of β -naphthol depends on time and temperature, being directly proportional to the product of the concentrations of naphthol and bisulfite, and does not depend on the ammonia concentration. The rate of amination may be expressed also as a function of the concentration of ammonium sulfite in the charge. In this case the reaction rate is directly proportional to the product of the concentrations of β -naphthol and sulfite and inversely proportional to the ammonia concentration.

SUMMARY

The kinetics of amination of β -naphthol has been studied, and the reaction scheme first proposed by N. N. Vorozhtsov has been fully confirmed.

LITERATURE CITED

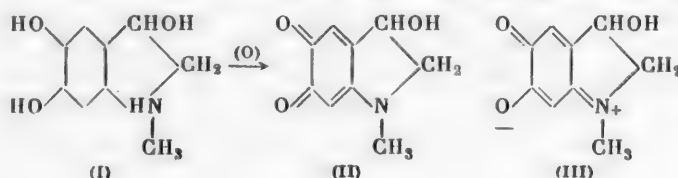
- [1] N. N. Vorozhtsov, J. Russ. Phys.-Chem. Soc. 47, 1669 (1915); Lieb. Ann. 381, 50 (1916); J. Russ. Phys.-Chem. Soc. 61, 483 (1929); Ber. 62, 57, 68 (1929); W. Fuchs, Ber. 54, 249 (1921); F. Raschig, Ber. 59, 859, 2025 (1926); Lieb. Ann. 448, 265 (1926).
- [2] N. N. Vorozhtsov, Bull. Ivanovo-Voznesensk Polytech. Inst. 6, 125 (1922); Bull. Soc. Chim. (4), 35, 995 (1924); Iu. Ia. Mikhailenko, Wks. Moscow Inst. Chem. Tech. [Tr. MKhTI] 12, 19 (1941).
- [3] W. A. Cowdrey, J. Chem. Soc. 1046 (1946).
- [4] W. A. Cowdrey and C. N. Hinshelwood, J. Chem. Soc. 1036 (1946); W. A. Cowdrey, J. Chem. Soc. 1041, 1044, 1046 (1946).

SYNTHESIS OF CERTAIN DERIVATIVES OF ADRENALIN

II. D,L-ADRENOCHROME OXIME AND SEMICARBAZONE

A. L. Remizov

Among the oxidation products of L-adrenalin (I), that having the greatest theoretical and practical interest is the so-called adrenochrome, which is customarily represented by structural formula (II) [1].



However, formula (II) is not in accord with the actual properties of this compound in which, for instance, only the carbonyl group can be found, since in contrast to other o-quinones it gives only monocarbonyl derivatives (monooxime, monosemicarbazone, monohydrazone). Its other chemical and physicochemical properties (color, solubility, etc.) do not correspond to structure (II), either. On this basis Harley-Mason [2] proposed for it the structure of zwitterion (III), which differs from (II) only in the disposition of the double bonds, so that the question here is that of the density distribution of the electron cloud.

Owing to its interesting physiological properties, L-adrenochrome has attracted a great deal of attention from pharmacologists [3], the very unstable quinone proving to be replaceable for pharmacological purposes by its completely stable monocarbonyl derivatives, the monooxime and monosemicarbazone. Of these, the latter, widely known in the foreign literature under the name "adrenoxyl," proved to be the more interesting.

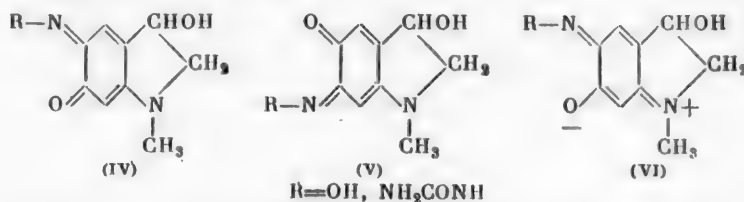
The preparation of the oxime and especially the semicarbazone from L-adrenochrome has been described many times, the published directions being very similar [1, 5-9]. The yield of the semicarbazone, according to literature data, does not exceed 40%, based on adrenochrome, the yield of which, in turn, scarcely comes to 50%, based on adrenalin. Data on the yield of the oxime are lacking. The preparation of certain derivatives of adrenochrome directly from adrenalin, which was oxidized in aqueous solution, is also described [10, 11].

In the present paper a description of the synthesis of the monooxime and monosemicarbazone of racemic adrenochrome and the results of an investigation of some of their properties are given. Neither of them has been examined pharmacologically to any appreciable extent [4], and no data on their synthesis and properties have been published.

We oxidized D,L-adrenalin in an aqueous medium with potassium ferricyanide [12], after which semicarbazide or hydroxylamine was added to the resulting solution of adrenochrome, and the corresponding mono-derivative was isolated in 80% yield for the semicarbazone and 50% yield for the oxime.

Analysis of the properties of adrenochrome monooxime and monosemicarbazone permits certain conclusions to be drawn regarding the details of their structure, which has scarcely been discussed as yet, although the problem of structure is not solved. After the present work was finished, a paper appeared [13], containing new data relating to the structure of the semicarbazone, which agree in part with those obtained by us. Both the oxime and the semicarbazone of adrenochrome might be obtained in the form of the two nontautomeric isomers (IV) and (V).

On the basis of their properties it is not possible to choose between these two formulas, but both are unacceptable, because the impossibility of obtaining dicarbonyl derivatives of adrenochrome cannot be explained on the basis of either. If the zwitterion structure with quaternary onium nitrogen (III), proposed by Harley-Mason [2], is assumed for adrenochrome, the problem of the structure of its carbonyl derivatives is simply solved; compound (III) can form only a monoderivative of structure (VI).

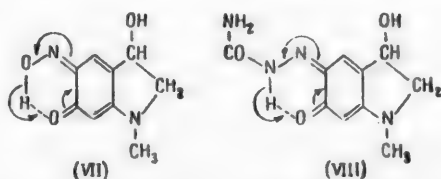


However, formula (VI) is at variance with a number of properties of the substances which it should represent. Primarily this regards the matter of their color. Solutions of adrenochrome in polar solvents (they are insoluble in nonpolar ones) have a cherry-red hue of high intensity, which may be explained, assuming that it has structure (III), by the presence of an ionized chromophore such as onium nitrogen attached to a quinoid ring by a double bond.* If the monooxime and monosemicarbazone had structure (VI), they would have to have a color of the same, or even greater, depth. Instead, a sharp hypsochromic effect is observed on their formation (both substances give orange-yellow solutions of no great intensity), which indicates a substantial difference between the electronic structures of the compounds being compared.

Certain chemical properties of the compounds being considered also are at variance with formula (VI). According to formula (VI) they must be zwitterions in which the cation is that of a strong quaternary ammonium base, and the anion is that of a weak, phenolic-type acid. The isoelectric point of such a zwitterion would have to lie in the alkaline region. However, potentiometric titration of adrenochrome monooxime and monosemicarbazone with alkali and acid in an aqueous medium showed that, although both are amphoteric, their basic properties are considerably weaker than their acid ones (Figs. 1 and 2). The fact that aqueous solutions of these compounds have not a basic, but rather an acid reaction is in accord with this. The apparent acid dissociation constants K_a , calculated from titration data, were found to be equal to $1.6 \cdot 10^{-11}$ ($pK_a = 10.8$) for the semicarbazone and $2.5 \cdot 10^{-9}$ ($pK_a = 8.6$) for the oxime. As regards the basic properties, they are so weak for both compounds that the corresponding constants could not be determined. Nevertheless, both substances could give fully characteristic, although not very stable, picrates, which were isolated by us and analyzed.

On the basis of their properties a structure similar to that of o-nitrophenol might be assumed for adrenochrome monooxime, whereas the structure of the monosemicarbazone might be considered to be like that of an o-oxyazo compound. With such a structure both of the compounds under consideration should be capable of forming an intramolecular hydrogen bond; this in turn should lead to a tendency to assume a benzoid structure instead of a quinoid one which apparently occurs in the original adrenochrome molecule.

This may be expressed in the form of formulas (VII) for the oxime and (VIII) for the semicarbazone.



Both (VII) and (VIII) should give chelate complexes with metals. Actually, as we have established, both the monooxime and the monosemicarbazone of adrenochrome can give such complexes with the ions Co^{2+} , Ni^{2+} , Cr^{3+} , Fe^{3+} and Fe^{2+} . Compounds with bivalent iron have a grassy-green color, whereas the rest have a reddish-orange hue many times more intense than that of the original compound. The color of the cobalt complex is distinguished by its peculiar intensity.

* The intense and deep color of aniline blue in polar solvents [14], for instance, is similarly explained.

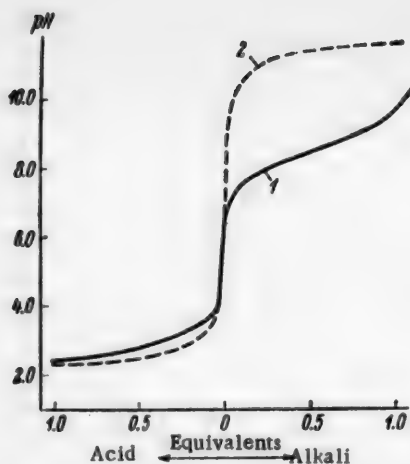


Fig. 1. Potentiometric titration curves.
1) Adrenochrome monooxime; 2) water.

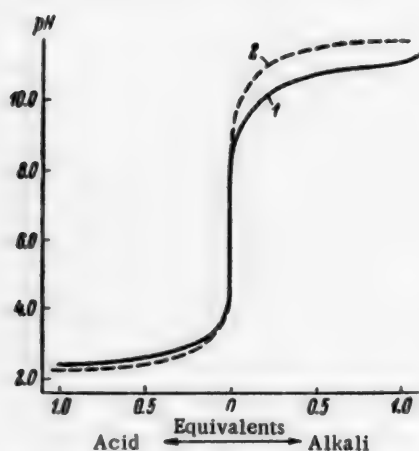
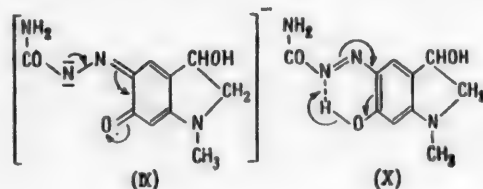


Fig. 2. Potentiometric titration curves.
1) Adrenochrome monosemicarbazone; 2) water.

Indirect arguments in favor of the above-stated hypothesis that the investigated compounds have structures (VII) and (VIII) were obtained on examination of their absorption spectra in neutral, acid, and alkaline media. In the spectrum of the neutral aqueous solution of the semicarbazone, two bands are readily distinguished (Fig. 3). One of them lies in the near ultraviolet region ($\lambda_{\max} = 3600 \text{ \AA}$, $\epsilon_{\max} = 2 \cdot 10^4$); the other, which is much less intense, is located in the visible part of the spectrum, in the 4200-4700 \AA range ($\epsilon_{\max} = 5 \cdot 10^3$), and causes the color of the solution. In an alkaline medium, where the semicarbazone is converted to the corresponding anion, the intense band is shifted from the ultraviolet to the visible region, its extinction increasing markedly ($\lambda_{\max} = 4450 \text{ \AA}$, $\epsilon_{\max} = 3.25 \cdot 10^4$). Changes of this kind in the absorption spectrum on ionization are characteristic of all phenols, as is generally known. It is customary to explain them by the enhancement of the electron-donor properties of the phenol oxygen on formation of the phenolate which for this reason acquires a tendency to assume the quinoid structure as a result of the displacement of electrons from the negatively charged oxygen to the benzene (and, in general, aromatic) ring.** If such an explanation is correct, the structure of the monosemicarbazone anion should be as shown in (IX), where the curved arrows indicate the direction of displacement of the electron cloud on delocalization of the negative charge of the ion, which undoubtedly must occur. The undissociated form of this compound, which absorbs in a shorter-wavelength region, would have to correspond to this to acquire structure (X).



Under the influence of the positively charged nitrogen of the dihydroindole ring, in an acid medium, electrons are shifted toward the middle, six-membered ring, which thereby acquires a still more "benzenoid" character. This is easily observable on the absorption curve; the band in the long-wave

part is smoothed out, but the absorption in the short-wave region increases. Similar conclusions may be drawn on interpretation of the absorption spectrum of adrenochrome monooxime (Fig. 4).

EXPERIMENTAL

D,L-Adrenochrome monosemicarbazone. A 2.75 g quantity (0.015 mole) of purified D,L-adrenalin [16] was dissolved in 30 ml of water and a sufficient amount of concentrated acetic acid (without excess). A solution of 19.5 g (0.06 mole) of potassium ferricyanide and 6.3 g (0.075 mole) of sodium bicarbonate in 80 ml of water was separately prepared, the first being dissolved on heating and the second being added in the cold. The prepared solution of oxidizing agent was added during 60-80 seconds to the vigorously stirred solution of adrenalin. The mixture immediately acquired an intense cherry-red hue and grew slightly warmer. After stirring for 5 minutes

*According to literature data [13], 4370 \AA .

**For example, see [15].

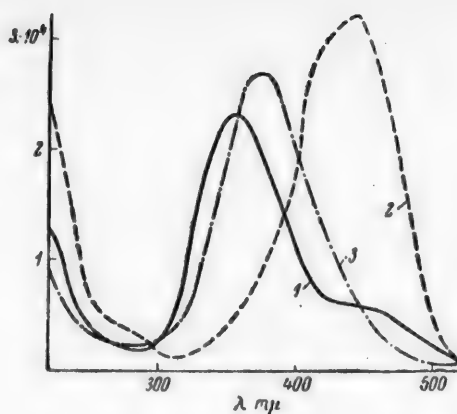


Fig. 3. Absorption spectrum of adrenochrome monosemicarbazone.

1) In water; 2) in 0.02 N NaOH; 3) in 0.08 N HCl.

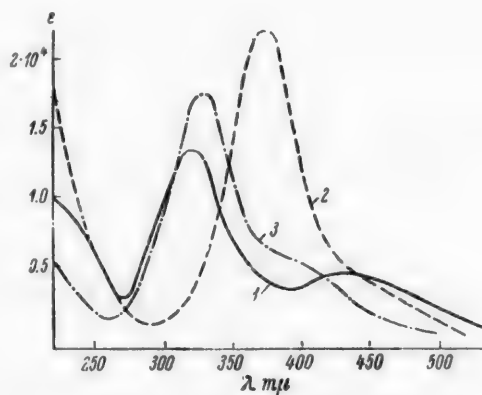


Fig. 4. Absorption spectrum of adrenochrome monooxime.

1) In water; 2) in 0.02 N NaOH; 3) in 0.08 N HCl.

a solution of 2.4 g (0.022 mole) of semicarbazide hydrochloride and 4.5 g of crystalline sodium acetate in 15 ml of water was added to it. To complete the reaction the liquid was stirred for 15 minutes at room temperature and then for 1.5-2 hours with cooling in an ice bath, after which the semicarbazone formed was filtered off, and washed in the filter with ice water until a pure orange-yellow filtrate was obtained. The precipitate, thoroughly pressed out on the filter, was then washed twice with an alcohol-ether (1:3) mixture and finally with pure ether. The yield of uncrystallized product with m.p. 218-220° (corr.) was 2.8 g (79%). After two crystallizations from water the compound melted with decomposition at 223° (corr.).

D,L-Adrenochrome monosemicarbazone is difficultly soluble in water (about 0.5 g in 1 liter at 20°), from which it crystallizes in the form of long, orange prisms with sharp edges, which do not contain solvent. It dissolves somewhat better in methanol, ethanol, or pyridine. Readily soluble in dilute alkali; soluble with more difficulty in dilute acid. It rapidly decomposes on heating in acid solution, turning brown.

Found % N 23.77, 23.65. $C_{10}H_{12}O_9N_4$. Calculated % N 23.72.

The picrate of the semicarbazone was obtained by mixing separately prepared hot solutions of 0.233 g of picric acid in 5 ml of water and 0.236 g of the semicarbazone in 20 ml of water (without striving for complete solution) and quickly filtering the still-hot mixture into a receiver placed in an ice bath, containing a small amount of the picrate for seed. The picrate formed was filtered off, washed on the filter with ice water (0.5 ml), an alcohol-ether mixture, (1:5), and ether. After drying in vacuo over sulfuric acid it had the form of a deep-yellow powder with a cryptocrystalline structure, which decomposes (partially melting) at a temperature near 150° and is difficultly soluble in water and readily soluble in methanol, ethanol, and acetone. On recrystallization from water it partly dissociates and is obtained in a mixture with the semicarbazone.

Found % N 21.27, 21.18. $C_{16}H_{16}O_{10}N_7$. Calculated % N 21.07.

D,L-Adrenochrome monooxime. To a solution of adrenochrome, prepared from 2.75 g of D,L-adrenalin (see above), was added a solution of 1.53 g (0.022 mole) of hydroxylamine hydrochloride and 4.5 g of crystalline sodium acetate in 15 ml of water. After stirring for 15 minutes at room temperature the mixture was left to stand for 1.5-2 hours in an ice bath, and the oxime formed was filtered off and washed with ice water until a light-orange filtrate was obtained, and then with an alcohol-ether mixture (1:5) and ether. The crude product was recrystallized twice from water and dried to constant weight at 100°. Yield 1.5-1.6 g (50-55%).

Racemic adrenochrome monooxime was isolated on recrystallization from water in the form of two crystal hydrates: short, deep-red prisms of the monohydrate, which separated out from hot, concentrated solutions, and long, thin, bright-orange needles of the dihydrate, which slowly separated out from cooled solutions. Both crystal hydrates were often obtained simultaneously. They have the same melting point, 178° (dec) (corr), and either is readily converted to the other on recrystallization.

Monohydrate. Found %: H_2O (by weight loss over P_2O_5) 8.50, 8.30; N 13.03, 13.48. $\text{C}_9\text{H}_{10}\text{O}_3\text{N}_2 \cdot \text{H}_2\text{O}$. Calculated %: H_2O 8.49; N 13.20.

Dihydrate. Found %: H_2O (by weight loss over P_2O_5) 15.63, 15.46; N 12.28. $\text{C}_9\text{H}_{10}\text{O}_3\text{N}_2 \cdot 2\text{H}_2\text{O}$. Calculated %: H_2O 15.64; N 12.17.

Anhydrous oxime. Found %: N 14.60, 14.55. $\text{C}_9\text{H}_{10}\text{O}_3\text{N}_2$. Calculated %: N 14.43.

The picrate of D,L-adrenochrome monooxime was obtained in the following manner. A 0.232 g portion of the oxime, twice recrystallized and dried over P_2O_5 , was dissolved by heating in 20 ml of water and mixed with a hot solution of 0.28 g of picric acid in 7 ml of water. On rapid cooling and vigorous trituration of the oil first formed, precipitate was obtained, which was filtered off and washed with ice water (0.5 ml), an alcohol-ether mixture (1:5), and ether. The yield of picrate, dried in vacuo over sulfuric acid, was 0.406 g (80%).

The picrate of the oxime is a light-yellow powder which decomposes, partly melting with marked darkening, at a temperature near 124° . It dissolves poorly in water, but better in the lower alcohols and acetone; it is insoluble in benzene and ether.

Found %: N 16.50, 16.44. $\text{C}_{15}\text{H}_{13}\text{O}_{10}\text{N}_5$. Calculated %: N 16.55.

Potentiometric titration of D,L-adrenochrome monooxime and monosemicarbazone. Either 0.118 g (0.5 millimole) of the monosemicarbazone or 0.098 g of the monooxime of D,L-adrenochrome was dissolved in 100 ml of freshly boiled, redistilled water, and the cautiously cooled supersaturated solution was titrated by means of a 0.05 N solution of NaOH or HCl, at 20° with glass and calomel electrodes. The PL-5 vacuum-tube voltmeter (pH meter) of the GIPKh* system was used for emf measurement. The glass electrode was calibrated in the usual manner with standard buffer solutions. The same volume (100 ml) of solvent (freshly boiled, redistilled water) was similarly titrated with 0.05 N alkali and acid. The titration curves obtained are shown in Figs. 1 and 2.

The acid dissociation constants were calculated from the pH at the semiequivalence point; data for a blank which was run by titrating the same volume of pure water [17] were taken into account. For the semicarbazone, $\text{pH} = 10.7$ at the semiequivalence point. On titration of the same volume of water after addition of 0.5 equivalent of alkali (calculated for a sample of the titrated semicarbazone), $\text{pH} = 11.4$. Therefore $K_a = [\text{H}] = 10^{-10.7} - 10^{-11.4} = 1.6 \cdot 10^{-11}$ and $\text{p}K_a = 10.8$.

In the case of the monooxime the correction for water titration was negligible, since the pH at the semiequivalence point was 8.6, and $\text{p}K_a = 8.6$.

Since the measurements were performed in solutions with ionic strength less than 0.005, the corrections for ion activity did not exceed the experimental error, and the constants found may be considered to approximate the thermodynamic values.

Determination of the absorption spectra of D,L-adrenochrome monooxime and monosemicarbazone in aqueous solution. Three 2.5 ml portions of a 0.001 M solution of the compound were separately diluted to 50 ml with water, 0.02 N NaOH solution, and 0.08 N HCl solution. Light-absorption measurements were performed in the usual manner in the 2200-5400 Å range with a SF-4 spectrophotometer. The absorption curves are shown in Figs. 3 and 4 for D,L-adrenochrome monosemicarbazone and monooxime, respectively.

Preparation of complex ions (lakes) of D,L-adrenochrome monooxime and monosemicarbazone with metal salts. To 5 ml of a 0.005 M solution of the monooxime or monosemicarbazone in a 0.1 M solution of sodium acetate (prepared by heating in a water bath) was added 0.5 ml of a 0.05 M solution of the appropriate metal salt. The mixture was kept at $45-50^\circ$ for 20-30 minutes. In this case the original color of the orange-yellow solution of complex former changed and became many times more intense. After a day a lake precipitated. Lakes with nickel (from the sulfate), cobalt (from the nitrate), chromium (from chrome alum), ferric iron (from the chloride), and ferrous iron (from the sulfate) were obtained in this way. All the complexes were orange with a more or less (depending on the cation taken) red tinge, except the last, which was grassy green.

SUMMARY

1. A synthesis of D,L-adrenochrome monooxime and monosemicarbazone, on which there are almost no data in the literature, has been worked out and their properties investigated. The acid dissociation constants of these compounds have been determined from potentiometric titration data.

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2. The picrates of D,L-adrenochrome monooxime and monosemicarbazone, which are not described in the literature, have been prepared and analyzed.

3. On the basis of a comparison of the color and acid-base properties of adrenochrome and its oxime and semicarbazone, hypotheses on the probable structure of the latter are advanced.

LITERATURE CITED

- [1] D. Green and D. Richter, *Bioch. J.* 31, 566 (1937).
- [2] J. Harley-Mason, *Experientia*, 5, 307 (1948).
- [3] Z. M. Bacq, *Pharm. Rev.* II, J. Pharm. Exper. Ther. 95 (ii), 1 (1949).
- [4] C. Beaudet, P. Trabert and F. Henaux, *Arch. Intern. Physiol.* 57, 343 (1950).
- [5] W. Veer, *Rec. Trav. Chim.* 61, 638 (1942).
- [6] F. Braconier, H. Le Bihau and C. Beaudet, *Arch. Intern. Pharmacodyn.* 69, 181 (1943).
- [7] C. Runti, *Gazz.* 80, 21 (1950).
- [8] E. Macciotta, *Gazz.* 81, 485 (1951).
- [9] H. Sobotka and J. Austin, *J. Am. Chem. Soc.* 73, 3077 (1951).
- [10] J. Harley-Mason, *J. Chem. Soc.* 1276 (1950).
- [11] Belg. Pat. No. 505022; *C.A.* 48, 13718c (1954).
- [12] D. Bu'lock and J. Harley-Mason, *J. Chem. Soc.* 712 (1951).
- [13] F. Ramirez and R. Ostwalden, *J. Org. Ch.* 20, 1676 (1955).
- [14] K. Venkataraman, *Chemistry of Synthetic Dyes*, State Chem. Press, L., 381 (1956).*
- [15] *Ibid.*, pp. 289, 396.
- [16] A. L. Remizov, *J. Gen. Chem.* 28, 2530 (1958).**
- [17] *Physical Methods of Organic Chemistry*, Vol. 4. Edited by A. Weissberger, IL, 418 (1955). *

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DERIVATIVES OF BICYCLO(1,2,2)HEPTANE

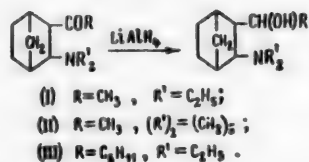
IV. SOME AMINES AND AMINOALCOHOLS OF THE BICYCLO(1,2,2)-HEPTANE SERIES

A. Ia. Khorlin, O. S. Chizhov and N. K. Kochetkov

Very recently amines of the bicyclo(1,2,2)heptane series have begun to attract attention because of the high physiological activity of some of them [1, 2]. Not long ago we described the synthesis of aminoketones of this series, namely certain derivatives of 2-acyl-3-dialkylaminobicyclo(1,2,2)heptanes [3]. In connection with the investigation, in progress in our laboratory, of the physiological activity of amines of the bicycloheptane series, we synthesized certain aminoalcohols and amines of this series, which, in the form of the hydrochlorides and alkiodides, were subjected to pharmacological investigation. It was of interest to follow the changes in physiological activity and, in particular, hypotensive action for compounds with the same bicyclo(1,2,2)heptane carbon skeleton and an amino group in position 3, resulting from replacement of the acyl radical in position 2 by a hydroxyalkyl or alkyl group.

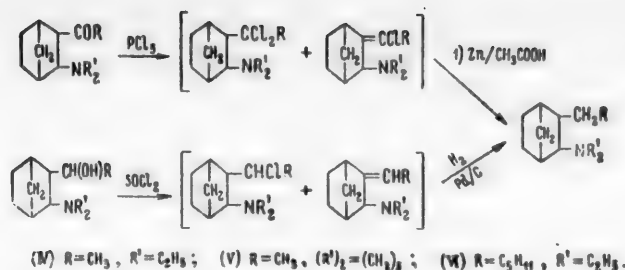
As was described in one of the preceding papers [3], the derivatives of 2-acyl-3-aminobicyclo(1,2,2)heptanes, which were used as starting materials in our work, are very smoothly obtained on treatment of readily accessible 2-acyl-3-chlorobicyclo(1,2,2)heptanes with secondary amines. At present we have synthesized, and in this article describe, three new members of this series: 2-caproyl-3-diethylamino-, 2-acetyl-3-dimethylamino-, and 2-acetyl-3-N-piperidylbicyclo(1,2,2)heptanes. The first of them was prepared according to the general directions [3], whereas the second was prepared in an autoclave, it being necessary to use pure dimethylamine, without difficulty. The preparation of the piperidine analog proved to be the simplest, since piperidine reacts very smoothly with 2-acetyl-3-chlorobicyclo(1,2,2)heptane even at room temperature, and the mixture was heated only to complete the reaction.

We converted the aminoketones of the bicycloheptane series to the corresponding aminoalcohols by reduction with lithium aluminum hydride.



The process goes very smoothly, and the corresponding aminoalcohols (I), (II) and (III), previously unknown, were obtained in nearly quantitative yields. They were viscous, noncrystallizing oils with a slight odor, which slowly darkened on keeping. Crystalline methiodides were prepared from them with no particular difficulty. The aminoalcohol hydrochlorides are extremely hygroscopic and are purified with difficulty; for pharmacological tests, therefore, solutions of them were prepared by exact neutralization of a portion of the aminoalcohol with dilute hydrochloric acid.

To obtain bicyclo(1,2,2)heptane derivatives of similar structure which do not contain oxygen functions, we tried two routes: from the corresponding aminoketones and from the aminoalcohols.



In the first route the aminoketone was treated with phosphorus pentachloride in chloroform solution, and the aminochloride hydrochloride thereby obtained as an oil was reduced, without purification, with zinc dust in acetic acid. However, the amine prepared by this method always contained a small percentage of chlorine and gave positive reactions for a double bond, evidently owing to admixture of an unsaturated chloride stable to reduction. By further hydrogenation of this slightly impure amine over palladium black, the pure amine was successfully prepared. We prepared 2-ethyl-3-diethylaminobicyclo(1,2,2)heptane (IV) from 2-acetyl-3-diethylaminobicyclo(1,2,2)heptane by this route with a yield about 40%.

Another route to amines of this type consists in the treatment of aminoalcohols with thionyl chloride; the substances so prepared contained about 3% chlorine and gave a pronounced reaction for the double bond. Thus the main reaction product resulting from the treatment of aminoalcohols with thionyl chloride obviously consisted of unsaturated amines containing admixtures of aminochlorides. We did not attempt to isolate individual substances from the mixtures obtained, but hydrogenated them directly in acetic acid over palladium on carbon. As a result pure amines were obtained with a yield about 40%. 2-Ethyl-3-N-piperidyl- and 2-hexyl-3-diethylaminobicyclo(1,2,2)heptanes (V) and (VI) were synthesized by this route. The amines obtained were oils with the typical, disagreeable odor of higher amines, which slowly darkened on keeping. We successfully prepared crystalline methiodides from amines (IV) and (V); amine (VI) gave an oily methiodide. The hydrochlorides of amines (IV), (V) and (VI) were prepared for pharmacological tests, similarly to those of aminoalcohols (I), (II) and (III).

The pharmacological investigation of the obtained aminoalcohols and amines of the bicyclo(1,2,2)heptane series, and also the corresponding aminoketones described in this and preceding articles [3], was conducted in the pharmacological division of the Iu. V. Uranov Institute of Pharmacology and Chemotherapy (in experiments with cats).

The tests showed that the hydrochlorides of amines, aminoalcohols, and aminoketones are devoid of ganglion-blocking action. On the contrary, aminoketone alkylidides (see [3]) have appreciable ganglion-blocking activity, while aminoalcohol and amine alkylidides manifest such activity only in particular cases, namely those cases where there is a radical containing only two carbon atoms in position 2 of the bicycloheptane ring. The lack of activity of piperidine derivatives is noteworthy.

As regards hypotensive activity, all the derivatives of aminoketones quite definitely lower the blood pressure by amounts which are sometimes considerable. Aminoalcohol alkylidides and hydrochlorides manifest only a feeble hypotensive effect. Most of the compounds which are active with respect to lowering the blood pressure have rather high toxicity.

EXPERIMENTAL

I. 2-Caproyl-3-chlorobicyclo(1,2,2)heptane was prepared by hydrogenation of 2-caproyl-3-chlorobicyclo(1,2,2)heptane-5 over Pd/BaSO₄ in acetone solution, as described earlier, [4], with a yield of 83.5%.

B.p. 132-134° (4 mm), d_4^{20} 1.0458, n_D^{20} 1.4823.

Found % Cl 15.11, 15.20. C₁₃H₂₁OCl. Calculated % Cl 15.43.

II. 2-Acetyl-3-dimethylaminobicyclo(1,2,2)heptane. A 15.0 g quantity of 2-acetyl-3-chlorobicyclo(1,2,2)heptane was mixed at -30° with 50 ml of dimethylamine, and the resulting mixture was heated in a metal ampule at 100° for 10 hours. Then the excess dimethylamine was evaporated and collected in a cooled trap, the residue was dissolved in 10% hydrochloric acid, the neutral substances were extracted with ether, the hydrochloric acid solution was made alkaline, the separated aminoketone was extracted with ether, and the extracts were dried

with potash and distilled. Yield 12.5 g (79.5%). Colorless liquid with a characteristic amine odor, which gradually darkens on keeping.

B.p. 106-108° (5 mm), d_4^{20} 0.9985, n_D^{20} 1.4850.

Found %: C 73.17, 73.13; H 10.17, 10.06. $C_{11}H_{19}ON$. Calculated %: C 72.88; H 10.56.

Methiodide colorless crystals with m.p. 164-166° (dec.) after reprecipitation from acetone by ether.

Found %: I 38.89, 38.91. $C_{12}H_{22}ON$. Calculated %: I 39.27.

Ethiodide, m.p. 158-160° (reprecipitated from acetone by ether).

Found %: I 37.61; 37.58. $C_{13}H_{24}ON$. Calculated %: I 37.68.

III. 2-Acetyl-3-N-piperidylbicyclo(1,2,2)heptane. A 17.0 g quantity of 2-acetyl-3-chlorobicyclo(1,2,2)heptane was mixed with 50 ml of piperidine. After 5-10 minutes strong, spontaneous heating of the mixture and copious precipitation of piperidine hydrochloride were observed. When spontaneous heating ceased, the reaction mass was heated in a boiling water bath for 3 hours, the excess pyridine was distilled off in vacuo, the residue was poured into water, and the aminoketone was isolated as described above. Yield 17.1 g (77%). Colorless, viscous oil with a characteristic, disagreeable odor; darkened on prolonged standing.

B.p. 120-122° (5 mm), d_4^{20} 1.0278, n_D^{20} 1.5052.

Found %: C 75.96, 75.68; H 10.22, $C_{14}H_{23}ON$. Calculated %: C 75.97; H 10.47.

Methiodide, m.p. 152-153° (purified through reprecipitation from acetone by ether).

IV. 2-Caproyl-3-diethylaminobicyclo(1,2,2)heptane was prepared by heating 22.9 g of 2-caproyl-3-chlorobicyclo(1,2,2)heptane and 75 ml of diethylamine for 10-15 hours according to the general method described earlier by us [3]. Yield 19.5 g (74%). Colorless oil with a characteristic, disagreeable odor, which turned yellow on keeping.

B.p. 127-129° (4 mm), d_4^{20} 0.9461, n_D^{20} 1.4775.

Found %: N 5.39, 5.63. $C_{17}H_{31}ON$. Calculated %: N 5.31.

Methiodide, m.p. 117-118° (purified through reprecipitation from acetone by ether).

Found %: I 31.46, 31.31. $C_{18}H_{34}ON$. Calculated %: I 31.16.

V. 2-(1-Hydroxyethyl)-3-diethylaminobicyclo(1,2,2)heptane. To a solution of lithium aluminum hydride prepared from 2.8 g of lithium hydride and 20 g of aluminum bromide in 100 ml of absolute ether, 31.0 g of 2-acetyl-3-diethylaminobicyclo(1,2,2)heptane was added, dropwise and with stirring, at such a rate that the reaction mixture boiled gently. The mixture was left for a day at room temperature, the excess lithium aluminum hydride was decomposed with alcohol, 300 ml of 40% sodium hydroxide was added, the ether layer was drawn off, the water layer was twice subjected to ether extraction, and the extracts were added to the main portion of the substance and dried with potash. The aminoalcohol was isolated by distillation. Yield 30.2 g (96%). A colorless, viscous liquid with a weak amine odor; it was kept for a long time without change.

B.p. 115-117° (3 mm), d_4^{20} 0.9694, n_D^{20} 1.4860.

Found %: C 73.58, 73.57; H 11.95, 11.64. $C_{19}H_{35}ON$. Calculated %: C 73.87; H 11.93.

The methiodide was prepared in the usual way and purified through reprecipitation from anhydrous acetone by ether; m.p. 149-150°.

Found %: I 35.90; 35.80. $C_{20}H_{39}ON$. Calculated %: I 35.92.

VI. 2-(1-Hydroxyethyl)-3-N-piperidylbicyclo(1,2,2)heptane. A 31.0 g quantity of 2-acetyl-3-N-piperidylbicyclo(1,2,2)heptane was reduced with lithium aluminum hydride (from 2.22 g of lithium hydride and 18.6 g of aluminum bromide) in 100 ml of absolute ether, as described in the preceding experiment. Yield of aminoalcohol, 29.2 g (93.5%). Colorless, very viscous oil with a weak amine odor; it gradually turned yellow on prolonged standing.

B.p. 139-141° (4 mm), n_D^{20} 1.5044.

Found %: C 75.30, 75.43; H 11.30, 11.23. $C_{24}H_{45}ON$. Calculated %: C 75.28; H 11.28.

Methiodide, m.p. 140-142° (from anhydrous acetone).

Found %: I 34.88, 34.90. $C_{15}H_{19}ON$. Calculated %: I 34.74.

VII. 2-(1-Hydroxyhexyl)-3-diethylaminobicyclo(1,2,2)heptane was similarly prepared from 26.5 g of 2-caproyl-3-diethylaminobicyclo(1,2,2)heptane by reduction with lithium aluminum hydride (from 1.6 g of lithium hydride and 13.4 g of aluminum bromide) in 60 ml of absolute ether. Yield 24.8 g (93%). Colorless oil which was kept for a long time without change.

B.p. 146-148° (3 mm), d_4^{20} 0.9382, n_D^{20} 1.4800.

Found %: C 76.59, 76.37; H 12.86, 12.90. $C_{17}H_{23}ON$. Calculated %: C 76.30; H 12.44.

The methiodide separated out in the form of an oil which crystallized on trituration with light petroleum ether. Colorless needles with m.p. 152.5-154° after reprecipitation from acetone by ether.

Found %: I 30.85, 30.79. $C_{18}H_{26}ON$. Calculated %: I 31.00.

VIII. 2-Ethyl-3-diethylaminobicyclo(1,2,2)heptane. To a suspension of 24.0 g of phosphorus pentachloride in 150 ml of dry chloroform was added 19.0 g of 2-acetyl-3-diethylaminobicyclo(1,2,2)heptane hydrochloride [3]. On stirring, the phosphorus pentachloride dissolved with slight heating, and the reaction mass turned orange. The mixture was stirred for 2 hours at room temperature, after which the solvent was distilled off in vacuo, the residue was shaken three times with absolute ether, and the ethereal solution was decanted from the oily hydrochloride. The 2-(1,1-dichloroethyl)-3-diethylaminobicyclo(1,2,2)heptane hydrochloride so obtained was dissolved in 150 ml of glacial acetic acid, and 40.0 g of zinc dust was added with stirring. When spontaneous heating ceased (about 0.5 hour), the mixture was heated with stirring in a boiling-water bath for 4 hours. Then the precipitate was filtered out, the mother liquor was poured into 400 ml of water, and the aqueous solution was shaken once with ether, in order to extract neutral substances, and made alkaline with solid sodium hydroxide. The amine which separated out was extracted with ether, and the extracts were dried with solid sodium hydroxide and distilled, the fraction with b.p. 107-112° (8 mm), n_D^{20} 1.4816 being collected; weight 12.4 g. The substance had a characteristic amine odor and decolorized a solution of bromine in carbon tetrachloride. It contained about 2% chlorine.

A 12.4 g quantity of the amine obtained was hydrogenated, without further purification, in 30 ml of glacial acetic acid over 1.0 g of palladium black. During 15 hours 1400 ml (0.063 mole) of hydrogen (0°, 760 mm) was absorbed, after which the hydrogenation was stopped. The catalyst was filtered out, the acetic acid solution was diluted with water, neutral substances were extracted with ether, the water layer was made alkaline, the separated amine was extracted with ether, and the extracts were dried with solid caustic and distilled. There was obtained 9.2 g (41%, calculated on the basis of the original aminoketone hydrochloride) of the amine. Colorless liquid with the characteristic odor of amines of the bicyclo(1,2,2)heptane series.

B.p. 73.5-74.5° (1 mm), d_4^{20} 0.9226, n_D^{20} 1.4770.

Found %: C 80.21, 80.09; H 12.65, 12.55. $C_{13}H_{23}N$. Calculated %: C 79.92; H 12.90.

The methiodide was purified through reprecipitation from acetone by ether; colorless leaflets with m.p. 176-176.5°.

Found %: I 37.73, 37.98. $C_{14}H_{23}N$. Calculated %: I 37.63.

IX. 2-Ethyl-3-N-piperidylbicyclo(1,2,2)heptane. To a solution of 6.3 ml of thionyl chloride in 30 ml of dry chloroform, 9.9 g of 2-(1-hydroxyethyl)-3-N-piperidylbicyclo(1,2,2)heptane was added dropwise during 15 minutes with stirring. The temperature of the reaction mass rose to 40-50°, and the latter turned brown. When the spontaneous heating ceased (1 hour), the mixture was boiled for 2 hours until the evolution of hydrogen chloride and sulfur dioxide had entirely stopped, the solvent and excess thionyl chloride were distilled off in vacuo, the residue was poured into water, and neutral substances were removed from the acidic, aqueous solution by extraction with ether. Then the aqueous solution was made alkaline, the separated amine was extracted with ether, and the extracts were dried with solid caustic and distilled. There was obtained 6.8 g of a mobile liquid with b.p. 118-120° (2 mm) and n_D^{20} 1.5060. The substance decolorized a solution of bromine in carbon tetrachloride and contained about 3% chlorine, being, therefore, a dehydration product of the aminoalcohol with an admixture of the aminochloride.

A 6.8 g quantity of the amine obtained, containing an admixture of the aminochloride, was hydrogenated in 20 ml of glacial acetic acid over 3.5 g of 10% palladium on carbon. During 12 hours 700 ml (0.0314 mole)

of hydrogen (0°, 760 mm) was absorbed, after which the hydrogenation was stopped. 2-Ethyl-3-N-piperidyl-bicyclo(1,2,2)heptane was isolated similarly to 2-ethyl-3-diethylaminobicyclo(1,2,2)heptane. There was obtained 3.2 g of the amine (37%, calculated on the basis of the original aminoalcohol). Colorless, mobile liquid with a characteristic amine odor. It was kept for a long time without change.

B.p. 115-117° (4 mm), d_4^{20} 0.9805, n_D^{20} 1.5040.

Found %: C 80.89, 81.17; H 12.28, 12.34. $C_{14}H_{25}N$. Calculated %: C 81.09; H 12.15.

Methiodide, m.p. 142-143° (reprecipitated from acetone by ether).

Found %: I 36.40, 36.57. $C_{15}H_{25}NI$. Calculated %: I 36.33.

X. 2-Hexyl-3-diethylaminobicyclo(1,2,2)heptane was prepared in a similar manner. From 13.0 g of 2-(1-hydroxyhexyl)-3-diethylaminobicyclo(1,2,2)heptane, after treatment with 10 ml of thionyl chloride in 70 ml of dry chloroform, there was obtained 10.2 g of a substance with b.p. 123-125° (1 mm), d_4^{20} 0.9131, n_D^{20} 1.4830, which decolorized a solution of bromine in carbon tetrachloride and contained about 3% chlorine.

On hydrogenation of the unsaturated amine, containing an admixture of the aminochloride, in 30 ml of glacial acetic acid over 4.0 g of 10% palladium on carbon, 930 ml (0.0415 mole) of hydrogen (0°, 760 mm) was absorbed during 10 hours. Yield 7.8 g (39.8%, calculated on the basis of the original aminoalcohol). Colorless liquid with a characteristic amine odor. It was kept for a long time without change.

B.p. 112-113° (1 mm), d_4^{20} 0.9032, n_D^{20} 1.4800.

Found %: C 81.20, 81.25; H 12.89, 13.02. $C_{17}H_{33}N$. Calculated %: C 81.20; H 13.22.

Hydrochloride and methiodide — oils which did not crystallize and could not be purified.

SUMMARY

1. 2-(1-Hydroxyalkyl)-3-dialkylaminobicyclo(1,2,2)heptanes have been prepared by the reduction of 2-acyl-3-dialkylaminobicyclo(1,2,2)heptanes with lithium aluminum hydride.

2. 2-Alkyl-3-dialkylaminobicyclo(1,2,2)heptanes have been prepared by two routes: a) treatment of 2-acyl-3-dialkylaminobicyclo(1,2,2)heptanes with phosphorus pentachloride, followed by reduction with zinc dust and hydrogenation, and b) treatment of 2-(1-hydroxyalkyl)-3-dialkylaminobicyclo(1,2,2)heptanes with thionyl chloride, followed by hydrogenation.

3. The question of the dependence of physiological action on structure in a series of amino derivatives of bicyclo(1,2,2)heptanes has been discussed.

LITERATURE CITED

- [1] Angew. Ch. 68, 4 (1956).
- [2] L. A. Stein, M. Slettinger, H. Arnold, D. Reinhold, W. Gaines and K. Pfister, J. Am. Chem. Soc. 78, 1514 (1956).
- [3] N. K. Kochetkov, A. Ia. Khorlin and O. S. Chizhov, J. Gen. Chem. 27, 1045 (1957). *
- [4] N. K. Kochetkov and A. Ia. Khorlin, J. Gen. Chem. 27, 3182 (1957). *

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